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THE INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on Wednesday, November 9, 1949: Dr E. B. Evans (Vice-President) was in the Chair.

The Minutes of the preceding Ordinary General Meeting, held on October 12, 1949, were read, confirmed, and signed.

The General Secretary (Mr D. A. Hough) announced the names of candidates elected to the various classes of membership since the last meeting of the Institute, and gave notice of the next meeting and of the Annual Dinner to be held on February 28, 1950.

Dr. E. B. Evans said: The petroleum industry covers a very wide range of interests, and when discussing the programme of meetings for each session endeavours are made to arrange, as far as possible, for a representative selection of some of the many topics to be included. This evening we have a series of papers on hydrocarbon chemistry, a subject which we do not often have the opportunity to discuss. The fundamental importance of hydrocarbon reactions and of an accurate knowledge of hydrocarbon properties needs no emphasis to anyone concerned with the production, utilization, or refining sides of the petroleum industry.

I hope those remarks may tend to reassure anyone who feels he may have strayed into a meeting of a society which, perhaps, discusses the finer points of organic chemistry rather more frequently than we do normally.

Our Chairman during the presentation and discussion of the papers this evening is Professor Frank Morton. Apart from his activities at Birmingham University, he has been connected with the research side of the petroleum industry for many years, and his work in the fields of organic and geo-chemistry is well known. In addition to being a Member of the Council of the Institute of Petroleum, he was previously Chairman of the Hydrocarbon Research Group, and is now Chairman of the Research Committee of the Institute. I am quite sure, therefore, that we could have no better Chairman for this evening's discussions. I have great pleasure in asking him to take the Chair.

Professor Frank Morton, formally occupying the Chair, said: We are here to discuss the work of the Synthesis Panel of the Hydrocarbon Research Group of the Institute of Petroleum. When the Synthesis Panel were asked to provide a series of papers for this meeting, the secretary of the Panel was Mr R. A. Lowry, of the Anglo-Iranian Oil Company, Sunbury. Whilst in the course of preparations for this meeting Mr Lowry was taken ill, and he died almost immediately. He was one of the younger and brilliant members in the industry, a man whom this Institute and the country could ill afford to lose; he will be missed by his many friends in the petroleum industry, and particularly by his colleagues at Sunbury.

May I ask you to stand in silence for a few moments as a token of our respect?

(The meeting observed a brief period of silence.)

The programme this evening is to be introduced by Dr Fidler, the Chairman of the Hydrocarbon Synthesis Panel. He needs no introduction to any audience in this Institute. The names of Birch, Dunstan, Fidler, Pim, and Tait are well known to you all by their contributions to the chemistry of the alkylation process; the original publication of the work of this Sunbury Group was, in my opinion, the greatest single contribution to the chemistry of hydrocarbons made in the decade preceding the war and, in its development to the full-scale plant, it was a major factor in our air offensive, being of the utmost importance in the manufacture of aviation fuels.

Dr Fidler was a founder member of the Panel, and its first secretary, and he succeeded his colleague, Dr Birch, as Chairman of the Panel in 1947. It is thus fitting that he should make the first statement of the Panel's work to the Institute, and I have very great pleasure in asking him to address us.

DR F. A. FIDLER: The Hydrocarbon Synthesis Panel, together with the Spectroscopic Panel and the Mass Spectrometry Panel, form the three working panels of the Hydrocarbon Research Group. This group continued the work which was originally sponsored by the Ministry of Aircraft Production during the war years.

The actual work of the Panels is carried out in university laboratories, and is sponsored by a number of industrial organizations. From 1944, when the Institute of Petroleum took over from the M.A.P., up to 1948 the members of the Synthesis Panel were engaged in preparing hydrocarbons required by the spectroscopists in connexion with their work of correlating structure with spectra. During this period, a considerable number of hydrocarbons were synthesized, particularly branched-chain paraffins and *cyclo*paraffins. However, a year ago, it was decided to widen considerably the scope of the work, and, instead of preparing a definite list of hydrocarbons, to carry out research into the general methods of synthesis and the reactions of hydrocarbons. This has had the effect of making the programme of work much more attractive to research workers in University laboratories. As will be realized from the papers to follow, the synthesis of hydrocarbons of known structure and purity is a highly specialized job which requires a considerable amount of patience to overcome the many unexpected snags which crop up in what appears a straightforward synthesis.

The necessity for carrying out work of this nature in this country is becoming of increasing importance. Not only are hydrocarbons of fundamental importance to the petroleum industry, but they are becoming of increasing value as raw materials in the chemical industry. A vast amount of research has been carried out in the States dealing with the preparation and properties of hydrocarbons, particularly under the auspices of the American Petroleum Institute. As a result of some of the research projects sponsored by the A.P.I., not only has a vast amount of fundamental information become available on hydrocarbons but also a set of standard hydrocarbons of known purity has become available for purchase. These hydrocarbons are of utmost value, since they allow a considerable saving in

time and are the generally accepted standards for spectrometer calibration. However, owing to the difficulty of obtaining these hydrocarbons under present conditions, it is of utmost importance that a similar bank of hydrocarbons be set up in Britain, and the work such as is being carried out by the Hydrocarbon Synthesis Panel should assist in bringing this about.

THE CHAIRMAN : I have now to introduce Dr C. R. Porter. Although Dr Porter was engaged in the synthesis of hydrocarbons under the M.A.P. sponsored programme, he did not officially join our Synthesis Panel until 1947, when he succeeded Dr Hickinbottom at Birmingham.

Dr Porter is I.C.I. Research Fellow in the Chemical Engineering Department of Birmingham University, and is perhaps best known for his analytical approach to problems in the field of hydrocarbon chemistry. At Birmingham he is also admired for the thoroughness of his approach to fundamental problems and for the delicacy of his manipulative technique.

DR PORTER then presented the following paper :

SOME GENERAL CONSIDERATIONS OF HYDROCARBON SYNTHESIS.

By C. R. PORTER.*

IN these researches on the synthesis of hydrocarbons, the aim was not merely to obtain specimens of the substances in question, but to obtain them in as pure a condition as possible, and by methods which left no reasonable doubt that they really were the substances alleged. These requirements naturally determined to a large extent the methods used. The aim of the present short paper is to outline some of the general principles which were continually borne in mind in Birmingham in planning and carrying out this work.

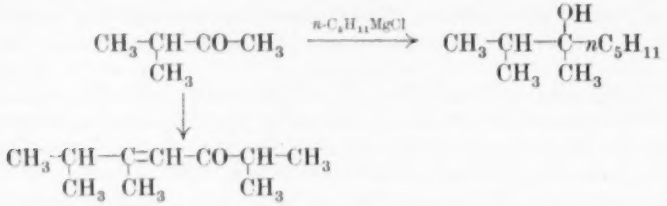
1. Practically all the hydrocarbons concerned were liquids of such molecular structure that they differed little in boiling point from possible impurities. In order to get as effective a fractionation as was reasonably possible, an endeavour was made to obtain not less than 100 ml of the final product. This usually involved commencing the synthesis on a rather larger scale than that to which academic workers are accustomed.

2. In view of the difficulty of purifying the hydrocarbons obtained in these quantities, intermediate products of the syntheses were themselves rigorously purified. As most of the intermediate products were also liquids, the main method of purification was fractional distillation, but adsorption and other processes were also used.

For instance, in the preparation of 2 : 3-dimethyloctanol-3 by the action of *n*-amyl magnesium chloride on methyl *iso*propyl ketone (Synthesis 5) a small amount of impurity was present which decolorized cold per-

* Dept. of Chemical Engineering, University of Birmingham.

manganate. This was probably 2 : 3 : 6-trimethylhept-3-ene-5-one formed by condensation of two molecules of methyl *iso*propyl ketone



This impurity boiled only 2° or 3° below that of the alcohol, and could not be separated by fractionation at 40 mm, with the column available, but was removed by adsorption on silica.

In view of the greater selectivity of crystallization as a method of purification, an endeavour was made to include at least one solid product in each synthesis, preferably as near the end as possible. This was frequently accomplished by conversion of the intermediate product into a solid derivative which could be reconverted into the original substance under very mild conditions.

Thus butyl, amyl, and hexyl alcohols, which were starting materials of several syntheses, were converted to the acid phthalates, these were re-crystallized to constant melting point, and then hydrolysed by a slight excess of dilute alkali. One or two alcohols (*e.g.*, 2 : 2 : 5-trimethylhexan-5-ol, an intermediate in the synthesis of 2 : 2 : 5-trimethylhexane (Synthesis 3) were purified by the formation and re-crystallization of their 3 : 5-dinitrobenzoates, but the hydrolysis of these esters required the use of fairly strong hot alkali, and the method was not subsequently used.

Some ketones, *e.g.*, methyl*iso*propylketone (Synthesis 5) were purified by conversion to the semicarbazones and hydrolysis of the latter with dilute acid. The tendency to form stable crystalline semicarbazones was found to decrease with increase of molecular weight of the ketone. *n*-Butyl-*sec*butyl ketone was obtained as an intermediate in the synthesis of 3 : 4-dimethyloctane (Synthesis 6). The semicarbazone from this ketone was found to be difficult to re-crystallize; as it appeared readily hydrolysed unless solvents were kept dry. In the preparation of alkyl benzenes, a number of toluidines and xylidines were purified through their acetyl derivatives.

Acids were purified through their amides or substituted amides, *e.g.*, *iso*butric through its amide, and *iso*caproic through its anilide.

As experience in the use of modern fractional-distillation equipment increased, more reliance began to be placed in this method of purification. The method of making solid derivatives followed by reconversion is accompanied sometimes with a feeling of doubt as to whether there is any impurity introduced during reconversion; also re-crystallization to constant melting point is not always adequate evidence of purity. For instance, *iso*caproic anilide, prepared from fermentation amyl alcohol (Synthesis 10) via the chloride and cyanide, required about six re-crystallizations to reach constant melting point; but a further six were required before the

acid was optically inactive, although the melting point was not raised by this further purification.

3. In planning syntheses, at each stage reactions were chosen, if possible, in which by-products likely to be formed would be easily separable from the required material by reason of considerable differences of physical or chemical properties. In condensations of the Wurtz and Fittig, zinc dialkyl, or Grignard type, it is preferable that the two reacting components are of different molecular weight, so that the products can be easily separated by fractional distillation, etc. In the preparation of 2 : 3-dimethyloctanol-3 mentioned above (5), both reagents contained five carbon atoms, hence the difficulty of separating the by-product formed by condensation of 2 mols of the ketone from that formed from 1 mol each of ketone and Grignard.

Again, in the preparation of *iso*butyl halides, it was possible to remove the last traces of the tertiary products formed at the same time by reason of the more ready hydrolysis of the latter.

4. Reactions were chosen as far as possible in which the molecular structures of the products could be predicted with reasonable certainty.

The preparation and dehydration of tertiary alcohols to the corresponding olefins was the method used in the synthesis of a number of olefins. 2 : 2 : 3-trimethylpentanol-3 (Synthesis 1), 2 : 3 : 3-trimethylpentanol-2 (Synthesis 2), 2 : 2 : 5-trimethylhexanol-5 (Synthesis 3), 2 : 2 : 6-trimethylheptanol-6 (Synthesis 8), 2 : 3-dimethyloctanol-3 (Synthesis 5), 3 : 4-dimethyloctanol-4 (Synthesis 6), and 2 : 2 : 4-trimethylhexanol-4 were all dehydrated to the corresponding olefins and hydrogenated to give the appropriate paraffins. Similarly 2 : 2-dimethylbutanol-3 was dehydrated to 2 : 2-dimethylbutene-3 for use in the synthesis of 2 : 2 : 5-trimethylhexane (Synthesis 3).

In such dehydrations, change in the carbon skeleton, particularly migration of methyl groups, sometimes takes place. For instance, it is well known that 2 : 2 : 3-trimethylpentanol-3 on treatment with iodine gives some 2 : 3 : 3-trimethylpentene-3; similarly pinacolyl alcohol gives some 2 : 3-dimethyl butene. These cases are largely predictable, and the course of the reaction may be changed by careful choice of reaction conditions. In the two cases referred to, no re-arrangement takes place if the dehydration is carried out by means of acetic anhydride and sodium acetate, or by heating with phthalic anhydride; at Birmingham these have been made the standard methods for dehydrating tertiary alcohols.

The addition of hydrogen bromide to olefins can frequently be made to take place in either sense at will, by choice of conditions. In the absence of air or oxidizing agents, the halogen adds on to the carbon atom with the smallest number of hydrogen atoms, but this can be reversed by carrying out the reaction in the presence of small amounts of peroxides, when primary or secondary halides are formed.

2 : 2-dimethylbutene-3 and 2 : 2-dimethylpentene-4 were by this method converted respectively into 1-bromo-3 : 3-dimethylbutane (Synthesis 3) and 1-bromo-4 : 4-dimethylpentane (Synthesis 8), which were then used in the synthesis of 2 : 2 : 5-trimethylhexane and 2 : 2 : 6-trimethylheptane.

In some reactions products of higher or lower molecular weight than the

required substance are formed, apparently without the formation of isomers. Di-*iso*-amyl ketone, formed as an intermediate in the synthesis of 2 : 8-dimethylnonane (Synthesis 10) was prepared by passing *iso*caproic acid over heated thoria. The product contained some methyl *iso*-amyl ketone, but this was easily separated from the main product, and no isomers appeared to be formed.

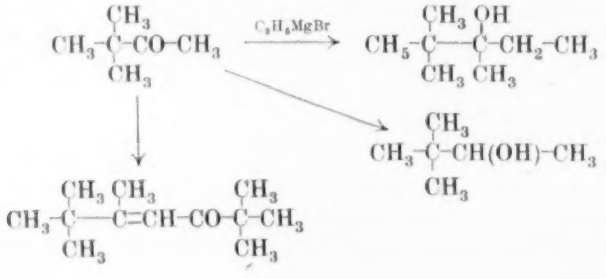
In replacement reaction substituents do not always enter quantitatively into the position previously occupied by the groups they replace. The usual preparation of *n*-amyl chloride from *n*-amyl alcohol is reported to give some *iso*-amyl chloride. This can be avoided by the use of thionyl chloride and pyridine as chlorinating agent (Synthesis 5).

It is reported that in the Wurtz–Fittig reaction the alkyl group does not always enter exclusively into the position previously occupied by the halogen atom. Preparations of 2-*n*-propyltoluene, 3- and 4-*n*-butyl toluenes, 4- and 5-ethyl-*m*-xylenes, 2-ethyl-*p*-xylene, and 1 : 3-diethyl benzene have not provided evidence of the formation of isomers.

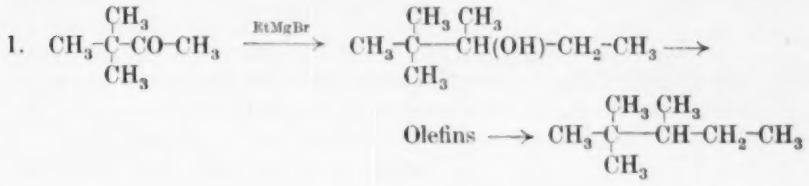
5. In order to keep the scale of operations in the initial stages of synthesis down to two or three kilos, it was more than ever necessary to search for reactions in which good yields were obtainable. This entailed considerable exploratory work before what appeared to be the best route decided upon, and in some cases where expected reactions failed to give adequate yields, syntheses had to be recommenced from the beginning.

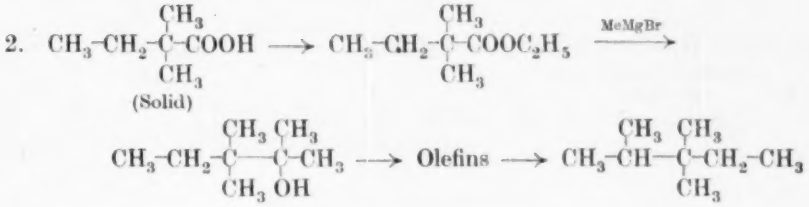
An attempt to prepare 2 : 3 : 3-trimethylheptane from 2-chloro-2-methylhexane and zinc di-*iso*propyl gave practically none of the desired product, although the zinc di-*iso*propyl was obtained in reasonable yield (9). This paraffin was subsequently prepared by the action of zinc di-*n*-butyl on 2 : 3-dimethyl-2-chlorobutane in 20–25 per cent yield (Synthesis 9). 2 : 3 : 3-trimethylhexane was prepared from the same tertiary chloride and zinc dipropyl in slightly higher yield (Synthesis 4). Hexane and hexenes appeared to be formed in fairly large amounts by reduction of or removal of hydrogen chloride from the 2 : 3-dimethyl-2-chlorobutane.

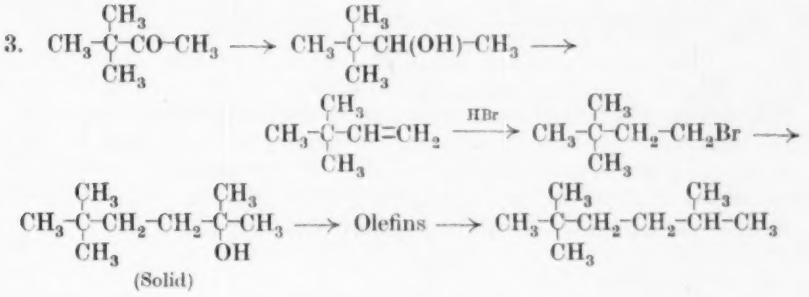
In preparations of tertiary alcohols from ketones or esters and Grignard reagents, the product was almost invariably contaminated by alcohols formed by the reduction of the ketone or ester. Where ketones were used, condensations of the mesityl oxide type also took place. Sometimes these substances were the main constituents of the products of these reactions. Ethyl magnesium bromide with pinacolone gave not only pinacolyl alcohol by reduction, but also 2 : 2 : 3 : 6 : 6-pentamethylhept-3-ene-5-one by condensation of 2 mols of the ketone (Synthesis 1).

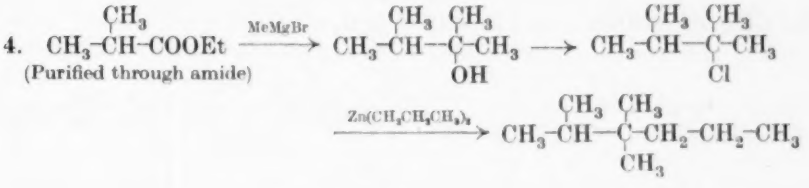


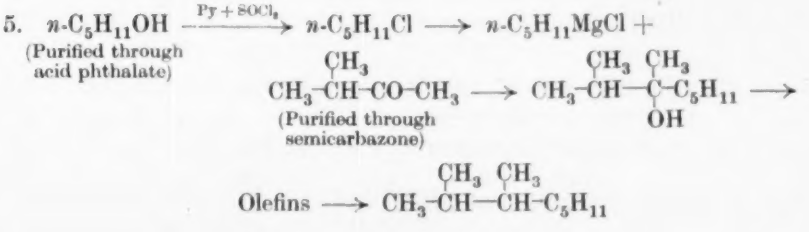
When *tert*-butyl magnesium chloride was used, the unsaturated ketone was practically the sole product of the reaction.











6. $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}(OH) \longrightarrow CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-COOH \longrightarrow$

(Purified through acid phthalate)

$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-COCl \xrightarrow{Cd(CH_3-CH_2-CH_2-CH_2)_2}$$

$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CO-C_4H_9 \xrightarrow{MeMgBr} CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{C}}(CH_3)-C_4H_9 \longrightarrow$$

(Semicarbazone)

$$\text{Olefins} \longrightarrow CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-C_4H_9$$

7. $CH_3-CH_2-CH_2-CH_2OH \longrightarrow C_4H_9MgCl \xrightarrow{CH_3COCH_3} C_4H_9-\underset{OH}{\underset{|}{C}}(CH_3)-CH_3 \longrightarrow$

(Purified through acid phthalate)

$$C_4H_9-\underset{Cl}{\underset{|}{C}}(CH_3)-CH_3 \xrightarrow{Zn(CH_3CH_2CH_3)_2} C_3H_7-\underset{CH_3}{\underset{|}{C}}(CH_3)-C_4H_9$$

8. $CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-CH_2-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-CH_2-CH_2-CH_2Br \longrightarrow$

$$CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-CH_2-CH_2-CH_2-COOH \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-CH_2-CH_2-CH_2-\underset{OH}{\underset{|}{C}}(CH_3)-CH_3 \longrightarrow$$

(Solid) (Solid)

$$\text{Olefins} \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-CH_2-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

9. $CH_3-\underset{CH_3}{\underset{|}{CH}}-COOEt \longrightarrow CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{C}}(CH_3)-CH_3 \xrightarrow{Zn(CH_3CH_2CH_2CH_3)_2}$

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{C}}(CH_3)-CH_2-CH_2-CH_2-CH_3$$

10. $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2(OH) \longrightarrow CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2Br \longrightarrow$

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-COOH \longrightarrow (CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2)_2CO \longrightarrow$$

(Purified through anilide)

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

THE CHAIRMAN: The next contribution is by Dr W. J. Hickinbottom, who was a founder member of the Panel, and has continued at Queen Mary College the work he commenced at Birmingham University. In addition to his work on the oxidation of olefins, he has been concerned with the synthesis of hydrocarbons containing a repeated pattern of quaternary groupings of carbon atoms. To this work he has brought a fund of new ideas and the enthusiasm necessary to carry them out. He leaves the Panel and his co-workers gasping at the scale on which he plans his attack, and he is rightly considered by the Group as one of the greatest workers in this most difficult field.

DR HICKINBOTTOM presented the following paper:

BRANCHED CHAIN HYDROCARBONS, THEIR SYNTHESIS AND REACTIONS.

By W. J. HICKINBOTTOM.

THE object of the work summarized in this paper is to develop methods for the synthesis of hydrocarbons with a repeating pattern of quaternary carbon atoms and side chains. There are indications that the physical properties and chemical reactions of such hydrocarbons might be of special interest. Furthermore, their structural relationship to the simpler polymerized olefins is sufficiently close to suggest that some information may be obtained about the nature and course of the polymerization of olefins.

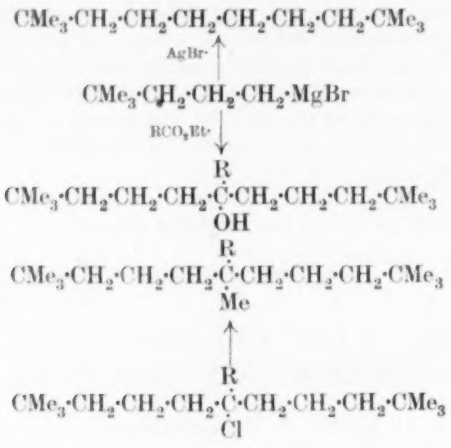
The standard method of preparing hydrocarbons with a quaternary carbon atom makes use of the reaction of zinc dialkyls or other organometal compounds with tertiary alkyl halides. This is of very restricted application to the present problems, and it became necessary to search for other methods. Two main lines of enquiry were decided upon: (*a*) the modification of compounds having a quaternary carbon atom to yield more complicated substances, and (*b*) the development of methods of introducing one or more quaternary carbon atoms into a preformed carbon chain.

A profitable line of approach to the first of these schemes appeared to lie in the application of the Grignard reaction. If primary alkyl halides having a highly branched structure can yield Grignard compounds, it should be possible to double the molecule by reaction with silver bromide or to obtain, by reaction with suitable esters, tertiary alcohols capable of modification to give hydrocarbons or of permitting the formation of a new quaternary group. The following substances were selected for model experiments.

(i) $CMe_3 \cdot CH_2 \cdot CH_2Br$ (ii) $CMe_3 \cdot CH_2 \cdot CH_2 \cdot CH_2Br$
(iii) $CEtMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Br$ (iv) $CMe_3 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH_2Cl$

It has been found that all these halides form Grignard compounds and

that they can be employed for the purposes required. The following scheme illustrates the general pattern of these syntheses :—



The following list gives some of the compounds which have been prepared.

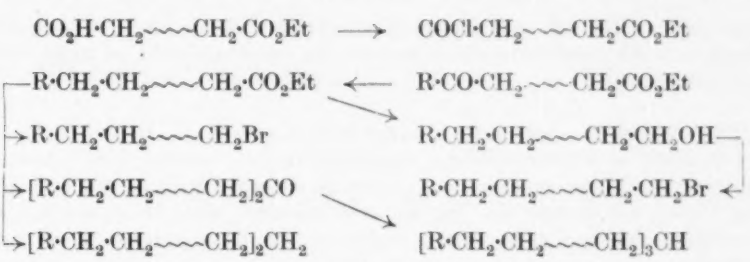
2 : 2 : 9 : 9-Tetramethyldecane.
3 : 3 : 10 : 10-Tetramethyldodecane.
2 : 2 : 4 : 9 : 11 : 11-Hexamethyldodecane.
2 : 2 : 15 : 15-Tetramethylhexadecane.
2 : 2 : 4 : 7 : 10 : 12 : 12-Heptamethyltridecane.
2 : 2 : 10 : 10-Tetramethyl-6-(4′ : 4′-dimethylpentyl)-undecane.
2 : 2 : 4 : 10 : 12 : 12-Hexamethyl-7-(3′ : 5′ : 5′-trimethylhexyl)-tridecane.
2 : 2 : 6 : 6-Tetramethyloctane.

The results of this preliminary work have been sufficiently promising to justify an extension of the programme to the preparation of more complicated halides which may serve as starting points for further syntheses of this type. Such halides can be represented by the general formula

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}CR'_2{\cdot}CH_2 \ . \ . \ . \ (CH_2{\cdot}CR'_2{\cdot}CH_2)_n \ . \ . \ . \ CH_2Br$$

(R = H, Me, CMe_3, etc. R′ = Me, Et, CMe_3, $CMe_3{\cdot}CH_2{\cdot}CH_2{\cdot}$, etc.).

One approach to the preparation of compounds of this type is the electrolysis of hemiesters. Thus $CO_2H{\cdot}CH_2{\cdot}CR_2{\cdot}CH_2{\cdot}CO_2Me$ should give $CO_2Me{\cdot}CH_2{\cdot}CR_2{\cdot}CH_2{\cdot}CH_2{\cdot}CR_2{\cdot}CH_2{\cdot}CO_2Me$. Modifications of the terminal groups would lead to compounds of the required type. In this phase of the work we were fortunate in having the experience of the Sunbury Research Station to help us in selecting suitable conditions for these electrolyses, and material is being collected for the subsequent stages of these syntheses. In the meanwhile, work is being carried out to select suitable methods of modifying the terminal groups. The scope of this phase of the work is illustrated by the following scheme :—



[$-CH_2\sim\sim\sim CH_2-$ represents a carbon chain with 2, 4, 6, 8 or more quaternary carbon atoms.]

An alternative method of increasing the chain length makes use of Kenner and Morton's method of decomposing the lead salts of carboxylic acids to give ketones. It is illustrated by the following scheme:

$$EtO_2C\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CO_2H \longrightarrow (EtO_2C\cdot CH_2\cdot CMe_2\cdot CH_2\cdot)_2CO$$

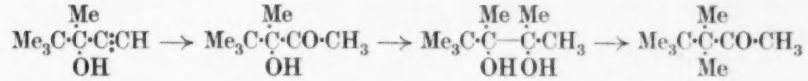
In the type of dibasic acid just discussed, the modification of the terminal groups is relatively simple compared with the problem when unsymmetrically substituted dibasic acids are under consideration. Here the situation is complicated by an equilibrium between the derivatives of the mono esters which excludes the application of the scheme of syntheses outlined above.

$$ClCO\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2Et$$
$$\downarrow\uparrow$$
$$EtO_2C\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot Cl$$

Accordingly, work is now in progress to develop methods of extending the carbon chain of unsymmetrically substituted acids in both directions and in such a way that there is no ambiguity about the structure of the resulting compounds. Attention is being concentrated on the preparation of keto-acids which might serve as suitable starting points. Some success has attended the formation of keto-acids from suitably substituted *cyclo*hexenes. If it is possible to overcome some of the difficulties in synthesizing *cyclo*hexenes of the required structure, this line of work may well be a profitable one.

The second of the major schemes of synthesis now in progress is concerned with the development of methods for inserting a quaternary carbon atom into a molecule already having one or more such carbon atoms.

One possible method makes use of the rearrangement of glycols. By selecting suitable starting points and methods, it should be possible to continue the process and extend the carbon chain. One such method, now being actively examined, is summarized by the following scheme :—



Some modifications have already been examined as in the formation 2 : 2 : 3 : 3-tetramethylbutanal from 2 : 2 : 4-trimethylpentan-3 : 4-diol. On the other hand, 2 : 2 : 3 : 4 : 5 : 5-hexamethyl hexan-3 : 4-diol does not

rearrange. Other glycols are being examined with a view to establishing the structural conditions which favour the rearrangement of highly substituted glycols.

THE CHAIRMAN: Our next speaker is Professor E. E. Turner, Professor of Chemistry at Bedford College, who needs no introduction to any chemical audience anywhere in the world. We may regard him as the father of this Panel, for it was his original collaboration with Dr Sutherland at Cambridge during the war which really set the whole programme of work in motion.

Professor Turner's work on a multitude of subjects over the last twenty-five years has been characterized by one outstanding feature—an insatiable curiosity. No matter what he sets out to do, he always asks why, and he ultimately provides the answer. So in the field of hydrocarbon synthesis, having produced a very large number of hydrocarbons at enormous speed, he wanted to know why some of these things gave certain results sometimes and other results in other cases. That led him on to the mechanism of the Grignard reaction.

He is a Fellow of the Royal Society, and he has one almost unique distinction, in that he is one of the few chemists who have been elected as Fellows of Queen Mary College.

It is a very great personal pleasure to me to welcome him to the rostrum of the Institute of Petroleum.

PROFESSOR TURNER introduced the two papers which follow by Mr H. J. Shine and himself and DR FIDLER presented the paper prepared by the late Mr R. A. Lowry, entitled "Purification of and the Determination of the Physical Properties of Hydrocarbons":—

THE SYNTHESIS OF 2:3:5-TRIMETHYLHEXANE AND OF 2:4:6-TRIMETHYLHEPTANE.*

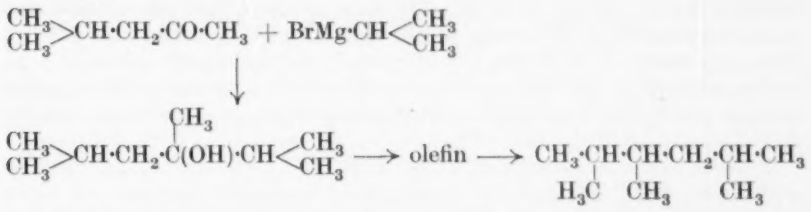
By H. J. SHINE and E. E. TURNER.

2:3:5-TRIMETHYLHEXANE was first prepared, although in an impure condition, by Silva.[1] A pure specimen was later obtained by Tuot [2] using the general scheme: *iso*propyl magnesium bromide + methyl *iso*butyl ketone ⟶ 2:3:5-trimethyl-hexan-3-ol ⟶ olefin ⟶ paraffin. Tuot gave the b.p. as 129°/738 mm. Howard *et al.*[3] prepared the hydrocarbon by reducing 2:3:5-trimethylhex-2-ene, this olefin being one of two products obtained by the action of *iso*propyl magnesium chloride on 1-chloro-2:3-dimethylbut-2-ene (the second product being 2:3:3:4-tetramethylpent-1-ene).

In the present work three different synthetic schemes have been explored:—

* Contribution from the Department of Chemistry, Bedford College, University of London.

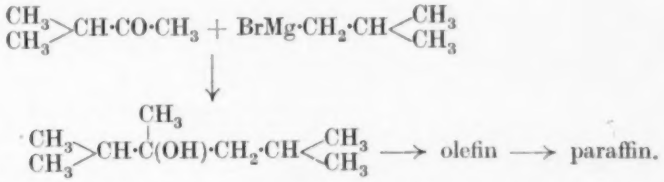
Scheme 1 :



In the first stage, seven experiments were conducted using from 1 to 4 gram-molecular quantities of ketone. Using the smaller quantity of ketone, the yield of pure carbinol varied from 22·5 to 26·5 g per 100 g (1 g. mol) of ketone. With the larger quantities less sharp fractionation was employed, 400 g of ketone giving 150 to 165 g of almost pure carbinol. The combined products were fractionated under reduced pressure, when, from 15 gram-mols of ketone, 230 g (10·7 per cent yield) of pure carbinol were isolated, b.p. 45·3°/3 mm, n_D^{20} 1·4321.

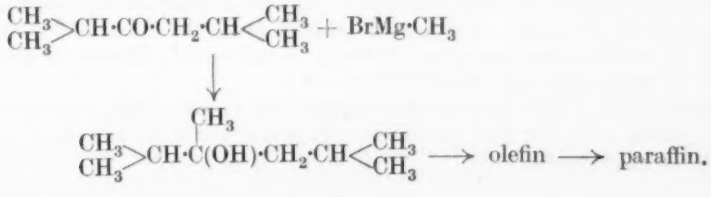
The carbinol was dehydrated by heating with naphthalene-β-sulphonic acid, or better by heating with anhydrous copper sulphate. In all, 230 g of carbinol were converted into olefin. The latter was reduced by hydrogen in glacial acetic acid in presence of Adams's platinum oxide catalyst, and the crude 2 : 3 : 5-trimethylhexane was twice distilled from sodium and then fractionated. 95 ml of pure 2 : 3 : 5-trimethylhexane were thus obtained, b.p. 130·5° to 130·7°/751 mm, n_D^{20} 1·4060 to 1·4061. Infra-red absorption measurements (Dr Sutherland) indicated that the material was uniform, as from first to last fractions.

Scheme 2 :



Only one experiment was carried out, since from 1 gram-molecule (86 g) of methyl *iso*propyl ketone only 25 g of crude carbinol were obtained. The synthesis is rendered unsuitable for other reasons : (1) methyl *iso*propyl ketone is difficult to prepare, and (2) preparation of pure *iso*butyl bromide in any quantity is tedious, and it is well known that *iso*butyl magnesium bromide leads to unwanted by-products.

Scheme 3 :

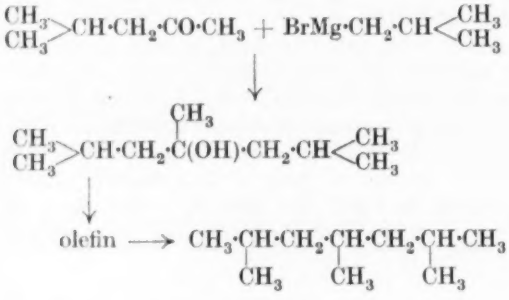


Here again, only one experiment was performed, 0·33 g.-mol of *iso*propyl *iso*butyl ketone giving 25 g of fairly pure carbinol, but the scheme was rendered unsatisfactory owing to the difficulty of preparing the ketone. Thus, (*a*) cadmium di-*iso*butyl (0·75 g.-mol) and *iso*butyryl chloride (1 g.-mol) gave only 14 per cent and 21 per cent yields of ketone in two separate runs, and (*b*) interaction of *iso*butyramide and *iso*propyl magnesium bromide gave 16 per cent of the desired ketone but 32 per cent of *iso*butyronitrile.

In order to obtain more information about the interaction of acid chlorides with cadmium di-*iso*butyl, the behaviour of the latter towards acetyl and propionyl chlorides was studied; 10 per cent of the calculated methyl *iso*butyl ketone and 26 per cent of the calculated ethyl *iso*butyl ketone were obtained.

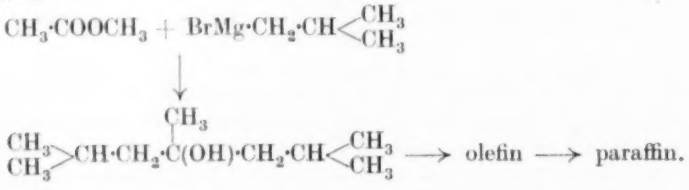
2 : 4 : 6-Trimethylheptane was prepared by Tuot.[2] Three routes to the hydrocarbon have been explored :—

Scheme 1 :



It was found that 0·4 g.-mol of ketone gave a 27 per cent yield of 2 : 4 : 6-trimethylheptan-4-ol. The scheme was regarded as unworkable owing to the (then) unavailability of methyl *iso*butyl ketone.

Scheme 2 :

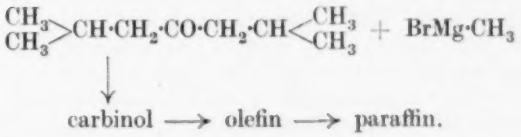


Eight experiments on the interaction of the ester and the Grignard reagent were performed, using quantities varying from 0·25 to 1 g. mol of ester.

It was found that the important conditions for a reasonable yield (33 per cent) were a high ratio of Grignard reagent (4 : 1) to ester, and a short period of heating subsequent to addition. Good initial yields were spoiled by too prolonged heating under reflux.

A total yield of 280 g of crude carbinol was accumulated, and this on fractionation gave 205 g of pure carbinol (overall yield, 18 per cent on the methyl acetate used).

Scheme 3 :



The product formed was an inseparable mixture.

The carbinol prepared by Scheme 2 was dehydrated by means of naphthalene-β-sulphonic acid and the olefin catalytically reduced (platinum oxide, acetic acid) to the paraffin. The 107 g of crude 2 : 4 : 6-trimethylheptane obtained were fractionated three times over sodium, the final b.p. being 145·2° to 147·4°/753 mm. In spite of the 2° range in b.p., the various fractions differed in refraction only from 1·4080 to 1·4084, and showed identical infra-red absorption (Dr Sutherland).

References.

[1] Silva. *Ber.*, 1872, **5**, 984.
[2] Tuot. *Compt. rend.*, 1933, **197**, 1434.
[3] Howard *et al.* *Bur. Standards J. Res., Wash.*, 1947, **38**, 374.

THE ANOMALOUS REACTIONS OF GRIGNARD REAGENTS (I).*

By H. J. Shine and E. E. Turner.

In 1946 [1] observations of the condensing and reducing properties of *iso*propyl magnesium bromide and *iso*butyl magnesium bromide when these reagents reacted with methyl *iso*butyl ketone were reported. It was also reported that methyl acetate gives the same reduction product, methyl *iso*butylcarbinol, when treated with *iso*butyl magnesium bromide as is obtained from methyl *iso*butyl ketone.

These observations led to an investigation of the " anomalous " reactions (generally recognized as reduction, enolization, and condensation) of Grignard reagents with carbonyl compounds, with the object of obtaining an understanding of why and how these reactions take place. These reactions will be referred to as the " anomalous " reactions, although they occur so frequently and to so large an extent that one might be tempted instead to describe the original Grignard addition reaction as anomalous. In this paper is presented a preliminary report of this work, giving at this time a more or less qualitative survey. The compounds used consist mainly of methyl ketones and of those Grignard reagents which give saturated and unsaturated gases as a consequence of anomalous reaction. The significance of the results reported in this paper will be discussed at a later date in the light of the gases evolved in anomalous reactions. At the moment it suffices to say that an understanding of these reactions cannot be obtained unless the *proportions* of reduction, enolization, and condensation be

* Contribution from the Department of Chemistry, Bedford College, University of London.

considered as well as the total amount of anomalous reaction each time a Grignard reagent reacts with a carbonyl compound.

It has been found that in every case the interaction of a Grignard reagent and a ketone is accompanied by reduction; each reaction is at the same time accompanied by either enolization or both enolization and condensation. The extent and kind of anomalous reaction depends on the structure of the reactants involved. It is believed particularly that enolization is a preliminary stage in condensation, the latter occurring if the spatial arrangement of the groups in the ketone permits. To illustrate these points the yields of products from some of the reactions are given in Table I. It must be made clear that the figures given are not precise. Although the product of each reaction was separated into fractions varying from twenty to forty in number, and the fractions were grouped on the values of their refractive indices, it was not possible to separate completely the four or five components of each reaction product. The losses due to the normal washing, extracting, and drying operations were increased by fractionation losses in working with products containing some components requiring fractionation

TABLE I.

*Products Obtained.**

RMgX.	Ketone.	Ketone.	Secondary carbinol.	Tertiary carbinol.	Dehydrated ketol.	Ketol.	Accounted percentage of original ketone used.
*n*PrMgBr	MeCO*n*Pr	—	5	70	5	—	80
*n*PrMgBr	MeCO*i*Bu	—	5	80	5	—	90
*i*PrMgBr	MeCOEt	—	5	30	35	—	75 †
*i*PrMgBr	MeCO*n*Pr	—	5	35	35	—	75
*i*PrMgBr	MeCO*i*Pr	—	—	10	50	—	60
*i*PrMgBr	MeCO*n*Bu	10	—	25	35	—	70
*i*PrMgBr	MeCO*i*Bu	5	5	20	60	—	90
*i*PrMgBr	MeCO*i*Bu §	5	—	25	50	—	80
*i*PrMgBr	MeCO*i*Bu ‖	—	15	25	40	—	80
*i*PrMgBr	MeCO*t*Bu	15	10	—	—	40	70 ‡
*i*PrMgBr	MeCO*n*Am	—	5	30	45	—	80
*i*PrMgBr	*i*PrCO*i*Pr	15	55	—	—	—	70
*i*PrMgBr	*i*BuCO*i*Bu	60	—	15	—	—	75
*i*PrMgCl	MeCO*t*Bu	40	5	—	—	35	80
*i*PrMgCl	MeCO*i*Bu	5	—	20	55	—	80
*i*BuMgBr	MeCO*n*Pr	—	50	25	—	—	75
*i*BuMgBr	MeCO*i*Bu	—	50	30	5	—	85
*i*BuMgBr	MeCO*i*Bu §	10	55	25	5	—	95
*i*BuMgBr	MeCO*t*Bu	—	65	—	—	30	95
*i*BuMgBr	*i*BuCO*i*Bu	5	65	20	—	—	90
*s*BuMgBr	MeCO*n*Pr	—	30	20	20	—	70
*s*BuMgBr	MeCO*i*Pr	10	20	—	40	—	70
*s*BuMgBr	MeCO*n*Bu	5	10	20	30	—	65
*s*BuMgBr	MeCO*i*Bu	5	10	15	55	—	85
*s*BuMgBr	MeCO*i*Bu §	10	10	15	60	—	95
*s*BuMgBr	MeCO*t*Bu	25	20	—	—	30	80 ‡
*s*BuMgBr	MeCO*n*Am	20	—	15	35	—	70
*s*BuMgCl	MeCO*t*Bu	35	10	—	—	35	80

* % based on ketone used.
† Includes 5% for the trimolecular condensate.
‡ Includes 5% for the reduced ketol.
§ Grignard solution maintained at −50°.
‖ 5 mol-% $CoCl_2$ added to Grignard solution maintained at 0°.

at atmospheric pressure and others requiring fractionation at reduced pressure. It is very probable that varying amounts of the low-boiling ketones and secondary carbinols were lost during the vacuum fractions. The figures in Table I are therefore given to the nearest 5 per cent.

Notwithstanding the insufficient accuracy of the figures, there are some conclusions that may be safely drawn. First, with methyl ketones, *iso*-propyl magnesium bromide causes more enolization (or condensation), but less reduction, than *iso*butyl magnesium bromide, while *sec*-butyl magnesium bromide lies between the two extremes. Second, not only is reduction by Grignard reagents influenced only slightly by low-temperature reaction, an observation already reported by Blicke and Powers,[2] and Kharasch and Weinhouse,[3] but enolization and condensation also are thus influenced only slightly. These observations do not support the postulations by a number of authors in the past that reduction (Rheinboldt and Roleff [4]) and enolization (Grignard and Savard [5]) are caused by the temperature-susceptible breakdown of an addition-complex. The addition-complex theories are again called in question by the effect of steric hindrance on anomalous reactions, examples of which have been given by Conant and Blatt [6] for reduction, and Whitmore *et al.*[7] for enolization, and are to be seen again in our results with di*iso*propyl ketone and di*iso*butyl ketone. It is interesting to note at this stage that whereas *iso*propyl magnesium bromide causes a goodly amount of reduction of di*iso*propyl ketone, its interaction with di*iso*butyl ketone follows more closely its interaction with the methyl ketones in causing a goodly amount of enolization.

The Products of Condensation.

In Table II are listed, with their characteristic properties, the condensation products obtained. Where it was possible to obtain a solid 2 : 4-dinitrophenylhydrazone by Brady's [8] method, its properties are given. It will be noticed that the 2 : 4-dinitrophenylhydrazone of methyl *iso*propyl ketone ketol is the same as that of the dehydrated ketol. It was found, too, that the 2 : 4-dinitrophenylhydrazone prepared from the ketol of methyl *t*-butyl ketone was really the derivative of the dehydrated ketol. This means that by using Brady's method the ketols are dehydrated at their tertiary hydroxyl group.

There seems to be an exception to this, however, in the case of the trimolecular condensate of methyl ethyl ketone. Analysis of the condensate and its derivative show that the condensate has a formula $C_{12}H_{22}O$ and a probable structure :—

$$\begin{array}{l} CH_3\cdot CH_2\cdot C{=}CH\cdot C(OH)\cdot CH_2\cdot CH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad CH_3{-}CH_2\cdot CO\cdot CH_2\cdot CH_3 \end{array}$$

An analogous compound was obtained by Gorhan [15] by heating *n*-butyraldehyde with 16 per cent sulphuric acid, and is given the probable structure :—

$$\begin{array}{l} CH_3\cdot CH_2\cdot CH_2\cdot CH{=}C\cdot CH(OH)\cdot CH\cdot CHO \\ \qquad\qquad\qquad\qquad\quad | \qquad\quad | \\ \qquad\qquad\qquad\qquad CH_2\cdot CH_3{-}CH_2\cdot CH_3 \end{array}$$

Again, in the case of methyl ethyl ketone, it was found that the bis molecular condensate corresponding to the ketols of the other ketone-

TABLE II.

Products of Condensation.

Ketone.	No.	Condensate.	B.p., °C.	n_D^{20}.	"2:4-dinitrophenylhydrazone"
MeCOEt	1	$EtC(CH_3)=CH\cdot C(OH)(CH_2\cdot COEt)\cdot Et$	93–94 (2 mm)	1·4651	Yellow needles, m.p. 146–147°
MeCO*n*Pr	2	$nPrC(CH_3)=CH\cdot CO nPr$ *	63–65 (3 mm)	1·4515	Liquid
	3	$nPrC(CH_3)(OH)\cdot CH_2\cdot CO nPr$ †	63 (1 mm)	1·4390	Liquid
MeCO*i*Pr	4	$iPrC(CH_3)=CH\cdot CO iPr$ ‡	43–44 (2 mm)	1·4512	Golden cubes, m.p. 85°
	5	$iPrC(CH_3)(OH)\cdot CH_2\cdot CO iPr$ §	64–65 (2 mm)	1·4371	Golden cubes, m.p. 85°
MeCO*n*Bu	6	$nBuC(CH_3)=CH\cdot CO nBu$ †, ‡	83–84 (2 mm)	1·4555	Liquid
MeCO*i*Bu	7	$iBuC(CH_3)=CH\cdot CO iBu$ †, ‡	69–70 (3 mm)	1·4521	Bright red plates, m.p. 126–127°
	8	$iBuC(CH_3)(OH)\cdot CH_2\cdot CO iBu$ †, §	87 (3 mm)	1·4389	—
MeCO*t*Bu	9	$tBuC(CH_3)(OH)\cdot CH_2\cdot CO tBu$ §, ‖	80–81 (4 mm)	1·4436	Yellow needles, m.p. 147–148°
	10	$tBuC(CH_3)(OH)\cdot CH_2\cdot CH(OH) tBu$ ¶	m.p. 92–93	—	—
MeCO*n*Am	11	$nAmC(CH_3)=CH\cdot CO nAm$ †	110 (2 mm)	1·4550	Liquid

* Kon and Leton [9] prepared this by the action of propylzinc iodide on propylacrylyl chloride.

† Grignard and Fluchaire.[10] These were prepared by treating the corresponding ketones with bromomagnesium butoxide. This and allied work by the same authors was used to support the theory of condensation via the halogeno-alkoxide addition-complex in Grignard reactions.

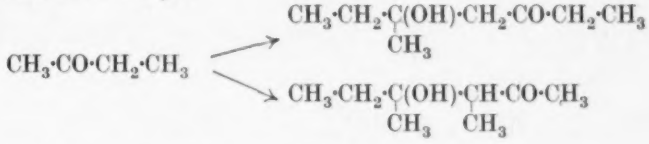
‡ Wayne and Adkins [11] prepared these by the action of aluminium *t*-butoxide on the corresponding ketones.

§ Colongé [12] prepared these by the action of methyl aminomagnesium bromide on the corresponding ketones.

‖ Tolstopyatov and Voroshilova [13] prepared this by the interaction of *t*-butyl magnesium chloride and pinacolone.

¶ Backer and Strating [14] reduced pinacolone ketol with sodium and ethyl alcohol.

consisted of two compounds. This was indicated in the preparation of the 2 : 4-dinitrophenylhydrazone. Two derivatives were obtained, but could not be separated completely. It is believed that with this ketone ketolization occurs in two ways :—



This would also account for the gradual drift of refractive index experienced when fractionating in the ketol region of the methyl ethyl ketone reaction products. The two ketols above would not differ very much in boiling point.

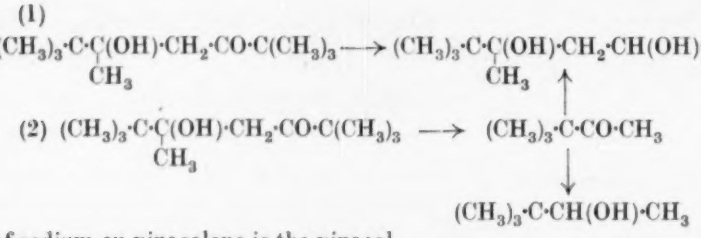
It is necessary to deal in more detail with the condensation products of methyl *t*-butyl ketone. Of the two recorded (see Table II) the second is the reduction product of the first. This reduction product was obtained from the residues of the reactions between pinacolone and (1) *iso*propyl magnesium bromide, and (2) *sec*-butyl magnesium bromide. Well-defined crystals formed in the cold residues, and were hardly in need of purification after they had been washed with a cold solvent. Although the solid product was obtained by the use of *iso*propyl and *sec*-butyl magnesium bromides, it was not obtained by the use of the corresponding chlorides.

When this solid product was first obtained it was thought to be a trimolecular condensate of pinacolone, since the liquid ketol had already been isolated from the same reaction. Analysis showed it to have the necessary empirical formula, but determination of the molecular weight showed this to be *ca* 200 instead of the 300 required by a trimolecular condensate. The molecular weight determinations also showed that the compound was associated in benzene and bromoform solutions.

The only recorded solid condensate of pinacolone is the pinacol, which was prepared by Delacre,[16] by the action of sodium on pinacolone in the presence of water. The m.p. recorded is 70° to 72°. The m.p. of the solid obtained from the Grignard reactions was 92° to 93°. It was impossible to oxidize this solid by Criegee's method, indicating that it was not a glycol. Since pinacolone pinacol could not be prepared by the method for other pinacols given by Gomberg and Bachmann,[17] the work of Delacre was repeated, and it was found that the recorded m.p. of 70° was correct.

It was found that the solid from the Grignard reactions could be dehydrated by distilling over naphthalene-2-sulphonic acid, did not form any of the common derivatives of primary or secondary alcohols, and did not form a 2 : 4-dinitrophenylhydrazone by Brady's method. Although dilute acids had no effect on the solid, concentrated nitric acid converted it to a liquid very similar to the product of the action of nitric acid on the ketol of pinacolone. Therefore the ketol was reduced with sodium and ethyl alcohol, and the two products were obtained : the solid, m.p. 92° to 93°, and pinacolyl alcohol. This meant that the solid could have been produced in two ways, either (1) by the direct reduction of the ketol, or (2) by the breakdown of the ketol to pinacolone, and the subsequent repolymerization of the pinacolone. The pinacolyl alcohol must have resulted from the

breakdown of the ketol, yet it was unlikely that the solid was produced by (2), since the only product beside pinacolyl alcohol that is obtained by the action



of sodium on pinacolone is the pinacol.

A similar reduction had been carried out by Backer and Strating,[14] who prepared pinacolone ketol by the method of Colongé,[14] and then reduced the ketol in benzene solution with sodium and ethyl alcohol. These authors reported m.p. 90° to 91°.

To verify that reduction (1) had occurred, the ketol was reduced by the method of Carothers and Adams,[18] involving hydrogen at 4 atm pressure and a platinum oxide catalyst activated with ferrous chloride. The solid, m.p. 92° to 93°, was obtained, and this m.p. was unaltered when some of this solid was mixed with some of that from the Grignard reactions.

A solid product was also obtained from the reaction of *iso*butyl magnesium bromide with pinacolone, but although this had a composition corresponding with the formula $(C_6H_{12}O)x$, it had m.p. 115°. Insufficient of this solid was obtained to permit of the determination of its molecular weight.

Experimental.

The Grignard Reactions. All the reagents used, whether purchased or made, were fractionated through a column of packed length 24 in, and internal dia 0·5 in, packed with Fenske helices, fitted with a total-reflux-variable-take-off still head, and insulated with an electrically heated asbestos jacket. These reagents then had a 1° boiling range at the appropriate b.p. The *iso*butyl bromide was also shaken with twice its volume of water for two successive periods of 12 hr each, to remove any residual *t*-butyl bromide, before finally drying over calcium chloride.

The procedure used in each of the Grignard reactions was as follows : The Grignard reagent was prepared in anhydrous ether (1250 ml) using pure magnesium (2 g atoms) and sufficient of the appropriate halide to dissolve the metal. At the end of the addition of the halide the solution was cooled and decanted through glass wool into a clean three-necked flask. To the Grignard solution was added 1 mol of the required ketone over a period of 2 to 3 hr, during which time stirring was maintained by a mercury sealed stirrer. (The flask was fitted with an outlet tube and traps to allow the collection of the gases evolved during reaction ; that part of the experimental work will not be described in this paper.) At the end of the addition of the ketone the solution was boiled under reflux for 1 hr, stirring being maintained. (The exceptions to this were the low-temperature reactions, carried out at − 50°, and the cobaltous chloride experiment, which were

allowed to stand and come to room temperature overnight.) The cooled solution was then hydrolysed by pouring on to crushed ice, dissolved out with hydrochloric acid, the two layers separated, and the aqueous layer extracted twice with ether. The combined ethereal solutions were washed once with 20 per cent sodium chloride solution, once with 10 per cent sodium hydroxide solution, and twice with water. After drying with potassium carbonate the ether was distilled off through an 8-in column packed with Fenske helices. The residue was then separated by vacuum distillation into two or three portions, depending on the reaction, and these portions were fractionated through a column of 12-in packed length, 0·4 in internal dia, packed with Fenske helices, fitted with a total-reflux-variable-take-off still head, and insulated with an electrically heated asbestos jacket. The tared receivers were designed to permit the collection of 0·5 to 10 g of distillate. Each fraction was weighed, and the refractive index of each was measured. Appropriate specimens were selected for analysis in each case. Those concerned in this paper are given in Table III.

TABLE III.

Condensate.	Analysis.				2 : 4-Dinitrophenylhydrazone.	Analysis.					
	Calcd.		Found.			Calcd.			Found.		
	C.	H.	C.	H.		C.	H.	N.	C.	H.	N.
1. $C_{12}H_{26}O_2$	72·7	11·2	71·5	12·1	$C_{18}H_{30}O_5N_4$	57·1	6·9	14·8	56·6	6·9	14·5
2. $C_{10}H_{18}O$	77·9	11·7	77·8	11·2							
3. $C_{10}H_{20}O_2$	69·7	11·7	69·9	11·3							
4. $C_{10}H_{18}O$	77·8	11·7	78·3	11·4	$C_{16}H_{22}O_4N_4$	57·5	6·6	16·7	57·5	6·6	16·4
5. $C_{10}H_{20}O_2$	68·7	11·7	69·9	11·7							
6. $C_{12}H_{22}O$	79·1	12·2	79·1	12·2							
7. $C_{12}H_{22}O$	79·1	12·2	79·3	12·1	$C_{18}H_{26}O_4N_4$	59·6	7·2	15·4	60·0	7·5	14·8
9. $C_{12}H_{24}O_2$	71·9	12·1	72·8	12·5	$C_{18}H_{26}O_4N_4$	59·6	7·2	15·4	59·9	7·3	15·1
10. $C_{12}H_{24}O_2$	71·2	12·9	71·3	12·7							
11. $C_{14}H_{28}O$	79·9	12·2	80·4	11·9							

$C_{12}H_{26}O_2$ from pinacolone. The residue from the fractionation of the product of reaction of *iso*propyl magnesium bromide and pinacolone crystallized on cooling and standing overnight. Drainage of the crystals at the water pump gave 8 g of fine white needles. Washing with petroleum ether at — 40° gave 6 g of crystals, m.p. 92° to 93°. Similarly, 5 g of the same material were obtained from the residue of the *sec*-butyl magnesium bromide–pinacolone reaction product. The molecular weight of the recrystallized material was determined at three concentrations in benzene solution, and the values obtained were extrapolated to zero concentration, giving a value of 210 for the molecular weight.

Reduction of pinacolone ketol (1). 4 g of the ketol were dissolved in 25 ml of ethyl alcohol, and 1 g of sodium was added in small pieces, with continual agitation of the solution. The solution was then cooled and diluted with water, which produced a small upper layer smelling of pinacolyl alcohol. Solid matter began to deposit, and the upper layer, on separation and evaporation, gave 2·5 g of white solid. Crystallization from aqueous ethyl alcohol gave m.p. 92° to 93°. A mixed m.p. with some of the solid from the Grignard reactions above was 92° to 93°.

Reduction of pinacolone ketol (2). Three and one half grams of the ketol were dissolved in 20 ml of ethyl alcohol, and 3 ml of N-ferric chloride were

added. The solution was shaken with Adams platinum oxide catalyst and hydrogen at a pressure of 50 p.s.i. for 12 hr. The filtered solution was diluted with water and extracted with ether. The ether extract was washed several times with water, and then dried over calcium chloride. Evaporation of the solution left a liquid residue, which slowly deposited crystals around its perimeter. These were removed, washed several times with cold ether, and recrystallized from aqueous ethyl alcohol, giving m.p. 92° to 93°. A mixed m.p. with some of the solid from the Grignard reactions above was 92° to 93°.

References.

[1] Shine and Turner. *Nature*, 1946, **158**, 170.
[2] Blicke and Powers. *J. Amer. chem. Soc.*, 1929, **51**, 3149.
[3] Kharasch and Weinhouse. *J. Org. Chem.*, 1936, **1**, 209.
[4] Rheinboldt and Roleff. *Ber.*, 1924, **57**, 1921. *J. Prakt. Chem.*, 1925, **109**, 175.
[5] Grignard and Savard. *Bull. Soc. Chim. Belg.*, 1927, **36**, 97.
[6] Conant and Blatt. *J. Amer. chem. Soc.*, 1929, **51**, 1227.
[7] Whitmore *et al.* *J. Amer. chem. Soc.*, 1942, **64**, 1239, 1242, 1247, 1251, 1618, 1619 and 2964.
[8] Brady. *J. Chem. Soc.*, 1931, 757.
[9] Kon and Leton. *J. Chem. Soc.*, 1931, 2946.
[10] Grignard and Fluchaire. *Ann. Chim. Phys.*, 1928, **9**, 5.
[11] Wayne and Adkins. *J. Amer. chem. Soc.*, 1940, **62**, 3401.
[12] Colongé. *Bull. Soc. chim.*, 1934, (v), **1**, 1101.
[13] Tolstopyatov and Voroshilova. *J. Gen. Chem.* (*U.S.S.R.*), 1945, **15**, 565.
[14] Backer and Strating. *Rec. Trav. Chim.*, 1937, **56**, 1069.
[15] Gorhan. *Monatsh.*, 1905, **26**, 82.
[16] Delacre. *Bull. Soc. chim.*, 1907, (iv), **1**, 536
[17] Gomberg and Bachmann. *J. Amer. chem. Soc.*, 1927, **49**, 237.
[18] Carothers and Adams. *J. Amer. chem. Soc.*, 1923, **45**, 1071.

PURIFICATION OF AND THE DETERMINATION OF THE PHYSICAL PROPERTIES OF HYDROCARBONS.

By (the late) R. A. Lowry.*

Previous papers this evening have discussed problems associated with reactions used for the preparation of hydrocarbons. The present paper deals with another aspect of hydrocarbons synthesis, namely the purification and characterization of hydrocarbons. This phase of the work is extremely important, and much of the benefit gained in surmounting difficulties in the synthesis may be lost if the final purification is not properly carried out or if the physical properties measured on the final sample are not determined with sufficient accuracy to be of value to other workers in the same field.

The confusing and unsatisfactory state of our knowledge ten years ago of the physical constants of even the simplest hydrocarbons can be seen by looking up the numerous alternative values given in the first two volumes of Egloff's "Physical Constants of Hydrocarbons." Fortunately, that position for the lower-boiling hydrocarbons has now been largely remedied, mainly by the efforts of the workers at the National Bureau of Standards in the United States. In fact, it is interesting to note that the physical

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data for the lower molecular weight hydrocarbons containing up to nine or ten carbon atoms are probably more complete and more accurate than for any other single class of organic compounds.

A considerable amount of work has been carried out in the last few years at numerous centres both in this country and the U.S.A. on the purification of hydrocarbons and the accurate determination of their physical constants. The two main sources of hydrocarbons are from purely synthetic sources or as concentrates obtained from some commercially available products. If bulk quantities of hydrocarbons are needed, then commercially available concentrates can be most valuable starting materials for the preparation of relatively pure hydrocarbons.

It must be realized that the ease of purification of hydrocarbons varies both with the individual hydrocarbon and also with its method of preparation. The latter is the reason for the emphasis which has been given this evening on the choice of route of synthesis and the careful purification of both starting materials and intermediates wherever possible. The hydrocarbon may be obtained only after a long and tedious synthesis, and therefore by the time it reaches the final stage, it is extremely valuable and as little as possible should be lost in the purification.

The final purity aimed at also has a most important bearing on the problem of purification. In certain cases it may be relatively easy to produce a particular hydrocarbon of 99·5 per cent purity, but to increase this to 99·95 per cent may be almost impossible unless one is prepared to discard 75 to 80 per cent of the material. It will be seen that by bringing about this increase in purity, one has reduced the percentage impurities by 90 per cent.

Since hydrocarbons are less prone to form solid derivatives than is the case with organic compounds containing oxygen, nitrogen, or sulphur, it is easy to realize why the majority of methods used for their purification are purely physical in character. The most widely used processes depend on distillation, and fractionation in high-efficiency columns is the most important tool yet available for hydrocarbon purification. So long as the hydrocarbon does not form constant boiling azeotropes with the impurities, this serves to remove any impurities save those of similar boiling point. The increase in efficiency in laboratory fractionating columns in the past ten to fifteen years has probably been the most important single reason for the improvement which has taken place in the availability of pure hydrocarbons. By increasing the efficiency of column packings, it has been possible to increase the ease of separation of closely boiling mixtures. It is not the purpose of this paper to discuss efficiency of fractionating columns, but such column packings as Fenske helices, Dixon gauze rings, Stedman gauze packing, and Podbielniak Heligrid packing are some of the materials which have been invaluable in helping to prepare samples of pure hydrocarbons. Fig. 1 shows a battery of typical laboratory distillation columns which are satisfactory for this particular purpose. A rather controversial problem has been the minimum quantity of hydrocarbon which can be purified satisfactorily. Most of the column packings mentioned above have relatively high hold-ups, and therefore in order to obtain full advantage of the efficiency of the packing, relatively large quantities of material are necessary for the fractionation. Thus, 1 to 2 litres or even larger should be

the quantity aimed at for the final hydrocarbon to enable it to be satisfactorily purified in columns such as those shown in Fig. 1. However, in many cases this is not possible, particularly in university research laboratories, where facilities are not always available for carrying out large-scale syntheses, and one had to be satisfied with much smaller quantities. Recently much effort has been concentrated on the development of columns which will handle small volumes of liquid, that is of the order of 10 to 20 ml. Examples of such columns are the spinning-band and concentric-tube type columns.

Now assume that the synthesis of a hydrocarbon has been completed. There is always the possibility that the crude product before fractionation contains traces of impurity of a completely different nature to the hydrocarbon itself. For instance, if it has been prepared by reduction of a ketone, it may contain small quantities of oxygenated materials. The presence of such impurities can complicate a fractionation, since they invariably lead to azeotrope formation between the impurity and desired hydrocarbon, and as a result give a slur in the distillation curve. Another common example is in the synthesis of paraffins, where the usual route is by hydrogenation of the corresponding olefin, and it may possibly be that traces of olefin are left in the hydrogenated product. The most satisfactory method of removing these trace impurities is to pass the hydrocarbon over an absorbent such as activated silica gel. This will serve to remove the olefin or any oxygen-containing impurity from the paraffin. In fact, a sound principle to adopt with all saturated hydrocarbons, *i.e.*, paraffins and *cyclo*paraffins, is to pass them over silica gel before the final fractionation.

In some cases, however, straight fractionation is insufficient to produce a hydrocarbon completely free of impurities. This may be due to the hydrocarbon and impurity having very similar boiling points or because they form constant boiling mixtures. This is often the case if the hydrocarbon has been produced from a concentrate which has become available from petroleum or coal-tar sources. For instance, the removal of small amounts of non-aromatic hydrocarbons from an aromatic of the same boiling point is a difficult separation to bring about. Fortunately, two other types of distillation are available, both of which have their own special advantages. These are azeotropic and extractive distillation. With the former, the impure hydrocarbon is distilled in mixture with a polar compound such as an alcohol or organic acid which acts as an entrainer. The polar compound should boil reasonably close to the hydrocarbon and have the power of forming an azeotrope with either the hydrocarbon or the impurity, or more usually with both. Then the boiling point difference between the azeotropes formed between the entrainer and the impurity should be sufficiently large to enable separation by distillation. Thus on the example quoted above, *i.e.*, the separation of small amounts of saturated hydrocarbons from an aromatic hydrocarbon of approximately the same boiling point, it is found that the non-aromatics form azeotropes with polar compounds such as alcohols, acids, etc., having lower boiling points than the azeotrope between the aromatic and the same entrainer. This therefore enables a separation to be effected by means of fractionation.

An alternative method of assisting the separation of hydrocarbons of different types but having the same boiling point, is extractive distillation

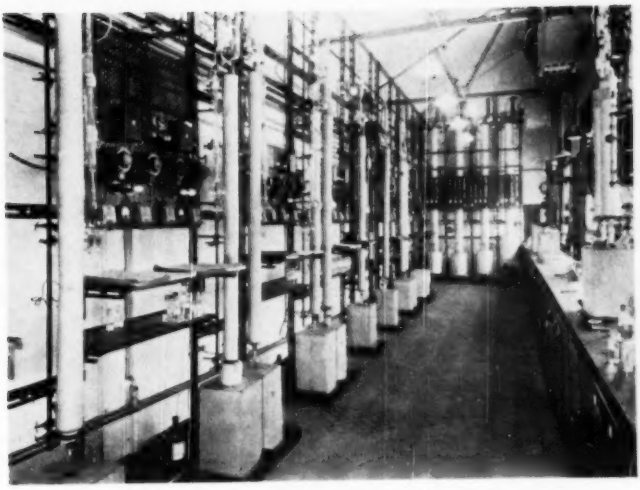

FIG. 1.

A SERIES OF LABORATORY FRACTIONATING COLUMNS.

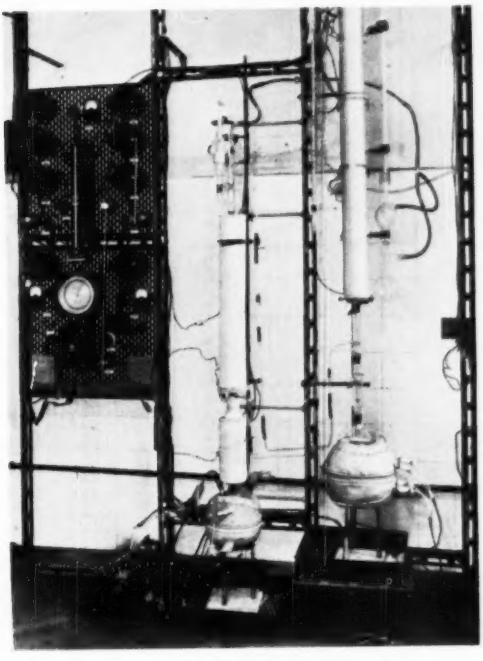

FIG. 2.

LABORATORY EXTRACTIVE DISTILLATION COLUMNS.

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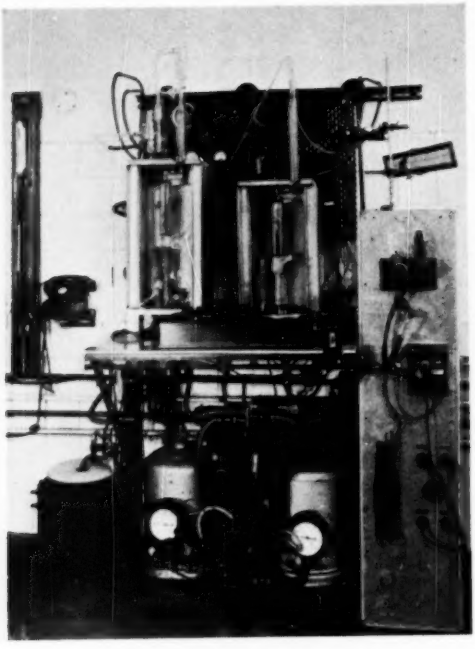

FIG. 3.

APPARATUS FOR DETERMINATION OF BOILING POINT AND VAPOUR PRESSURE–TEMPERATURE RELATIONSHIPS OF HYDROCARBONS.

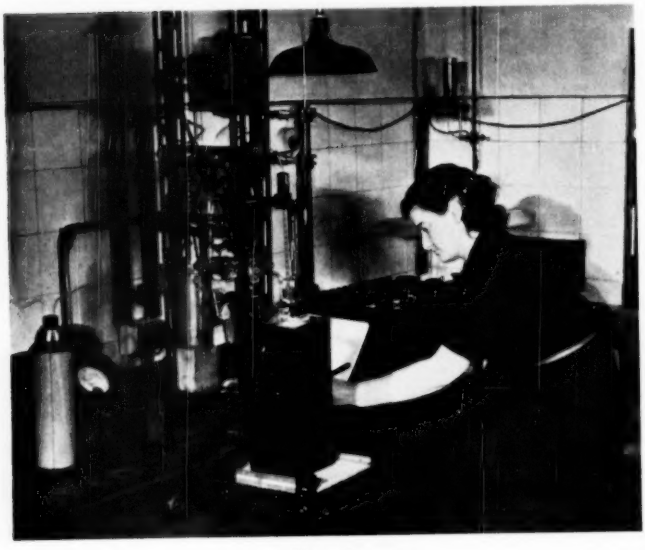

FIG. 4.

APPARATUS FOR THE DETERMINATION OF FREEZING POINT OF HYDROCARBONS.

or vapour–liquid extraction. This also employs a polar solvent, but in this case the solvent boils at a much higher temperature than the hydrocarbon, and for the purification of a hydrocarbon such as toluene, phenol, or aniline can be employed as suitable solvents. The solvent is allowed to flow down the column together with the hydrocarbon reflux and therefore washes the ascending hydrocarbon vapours. The solvent has the effect of increasing the relative volatility between them, and thus allows a separation to be effected. For instance, *cyclo*hexane and benzene have essentially the same volatility, but on addition of phenol or aniline, the volatility of *cyclo*hexane is considerably increased relative to that of benzene and distils over first. This method can thus be used as an alternative one to azeotropic distillation for the removal of small amounts of non-aromatic hydrocarbons from aromatics. However, it is most valuable as a means for separating paraffins and *cyclo*paraffins of the same boiling point. Fig. 2 shows a useful form of this type of column for laboratory use.

A method of purification which can on occasion be extremely valuable is fractional crystallization. It may occur that two isomers have almost identical boiling points but quite different freezing points. By employing fractional crystallization either from itself or from a solvent, it may be possible to remove small amounts of low-melting impurities from a high-melting hydrocarbon. A very good example of this is *p*-xylene, which has a freezing point almost 60° C higher than its close boiling isomer, *m*-xylene.

Since a considerable amount of effort may have been involved in synthesizing and purifying a hydrocarbon to achieve its final high state of purity, it is of utmost importance that its physical constants should be determined with as great an accuracy as possible. This then means that these constants can be used with confidence by other workers for the purpose of identification and comparison. Some of the properties are comparatively simple to determine. Provided an accurate refractometer is available for refractive-index measurements and a carefully calibrated pyknometer for densities, both these can be carried out on extremely small quantities of liquids. A point that must be stressed in making these two measurements is the necessity for carefully controlled temperature conditions. Literature references are occasionally found giving these properties to four or five places of decimals with no mention of the temperature at which the determinations were made. This, of course, renders the very careful work, which has obviously been carried out, quite useless from the point of view of reference by other workers. The usual temperatures which have become adopted as standard are 20° and 25° C for both refractive index and density. If possible, it is most useful to workers in the petroleum field to have the refractive index measured at several wavelengths.

For many purposes, the boiling point as registered at the top of a fractionating column is sufficiently accurate for most identification purposes. However, if the boiling point is to be determined with a high degree of accuracy, special precautions have to be taken and an apparatus such as that designed by Swietoslawski or at the National Bureau of Standards is required. With such an apparatus (Fig. 3), not only is one able to determine the boiling point of hydrocarbons at atmospheric pressure, but it also allows a study of the vapour pressure–temperature relationship over a wide range of pressures.

All these data are very useful, but in themselves they do not provide a criterion for the absolute purity of the final product unless the nature of the likely impurity is known. For instance, in the case of refractive index measurements, if accurate data are available for the value of the refractive index of the pure compound required and also of the impurity present, an estimation of the purity of the sample can be made by simple proportion. The data, however, are not very often available, and in any case with isomeric hydrocarbons the difference in such constants as refractive index, density, or boiling point between the various isomers is usually exceedingly small.

At this point the importance of the determination of freezing point must be stressed. In the first place the value of the freezing point depends more on the symmetry of the molecule than on its molecular weight, so that there is often a wide divergence in the freezing points of compounds which in other respects are very similar. Consider, for instance, the case of the four C_8 aromatics, ethylbenzene, *o*-, *m*- and *p*-xylene. *o*-Xylene is well characterized as it boils reasonably above the other three, but ethylbenzene and *m*- and *p*-xylene all boil within 3° C of each other, and they have a range of only 0·0014 in refractive index and 0·006 in density. The freezing points, however, have a range of over 100° C, so that a very simple apparatus would serve to identify an unknown C_8 aromatic.

Apart from this, the greatest use of the freezing point determination is in the estimation of purity. Dr F. D. Rossini and his co-workers at the Bureau of Standards in Washington have developed a method of determining the absolute purity of a sample from a time–temperature freezing curve which, with a skilled operator, can be performed as a routine test. The apparatus which has been developed for the determination of freezing points is shown in Fig. 4.

About 50 ml of sample are placed in a double-walled tube which is surrounded by a cooling bath of liquid nitrogen, solid CO_2–petroleum ether slush, or ice, according to the freezing temperature of the sample. The pressure between the walls of the tube is adjusted to give an initial cooling rate of about 0·3° C per minute. The sample is kept well stirred, and the temperature measurement is made by the most accurate means available. A platinum resistance thermometer or thermocouple measuring to 0·01° C, or if possible 0·001° C, is most suitable. The temperature is noted every minute, and the time–temperature curve drawn. For a material of 100 per cent purity the freezing curve will be horizontal during the period when crystallization is taking place, but as the purity decreases the freezing point is lowered and the curve, departing from horizontal, has been shown to take the form of a rectangular hyperbola. Assuming the impurity forms an ideal solution with the main component, the pure material crystallizes out first, leaving the impurity in the liquid phase. Thus, by the time the sample is half-frozen, the impurity in the material then freezing has doubled, so that the lowering in the equilibrium temperature between the initial freezing point and the point at which the sample is half-frozen corresponds to a doubling in impurity. The temperature at which the compound would have frozen had it been 100 per cent pure is then determined, being higher than the actual freezing point by this same amount. The mol per cent of impurity in the sample (N) can be calculated from the

approximate formula $N = A\Delta T$, where A is the cryoscopic constant, and ΔT is the depression of freezing point from that of a 100 per cent pure sample.

The cryoscopic constant involves a knowledge of the latent heat of fusion, which can be determined fairly easily in several ways if it is not already known.

A graphical method for extrapolating the freezing point and determining the freezing point for zero impurity has also been developed by Dr Rossini for use with compounds which super cool to a considerable extent before crystallization can be induced, or do not remain in thermodynamic equilibrium sufficiently long to enable a large enough portion of the curve to be drawn. The method for using this technique is shown in Fig. 5.

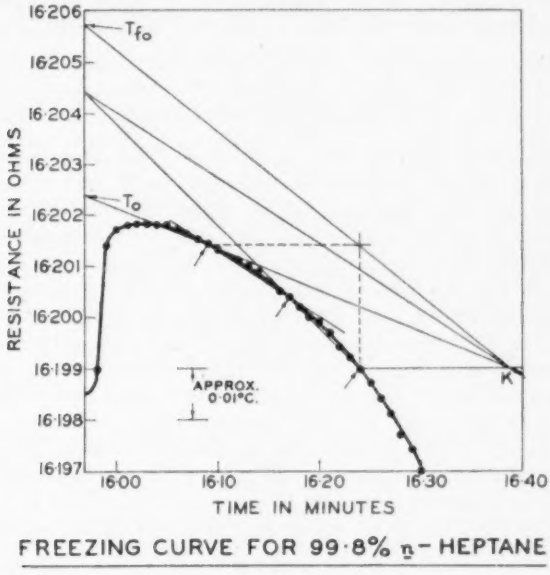

FIG. 5.

GRAPHICAL METHOD FOR DETERMINING FREEZING POINT OF HYDROCARBON FROM TIME–TEMPERATURE COOLING CURVE.

Thus for any hydrocarbon which can be made to crystallize and which gives a smooth time–temperature freezing or melting curve, an estimation of the absolute purity of the final product can be made.

Mention should be made here of a rather novel form of apparatus for determining the freezing points, and hence the purities of compounds which has recently been developed at the Chemical Research Laboratories at Teddington. The temperature measurements are made by means of themistors, and the time–temperature cooling curve is recorded automatically. In addition, the determination can be carried out on approximately 10 to 20 ml of liquid instead of the 50 to 60 ml required in the conventional Bureau of Standards apparatus. This has been achieved by applying a pulsating gas pressure to the liquid surface in such a way as to produce oscillation in a U-shaped column of the liquid being frozen. This form of

mixing avoids the use of a mechanical stirrer. Full details of this technique have recently been published in the *Journal of the Chemical Society*.

In conclusion, mention must be made of the increasing importance of spectroscopic data for identifying hydrocarbons and showing the presence of impurities. Characteristic peaks in the spectrograms of different compounds can often be determined to enable unknown mixtures to be analysed later. More detailed description of this is, however, beyond the scope of this paper.

It can be appreciated therefore that the actual synthesis of the hydrocarbon may sometimes be little more than half the work needed, and a great deal of effort can be profitably spent in working up the product to a high degree of purity and determining on the pure compound accurate physical constants which will often be of great value to other workers.

Discussion on the Papers.

H. C. Rampton: Having been a colleague of Mr R. A. Lowry for some years, I am naturally acquainted with his work, but rather from the analysis than from the synthesis angle. First, I would like to stress one point, however, which has come into prominence recently in America, and that is nomenclature. It is obvious, from the formulæ we have seen this evening, that the problem of naming hydrocarbons can become very complex, and therefore consideration should be given to some system, preferably international, so that no ambiguity can exist. A recent American Chemical Society meeting, embodying a joint symposium on Hydrocarbon Nomenclature (*Atlantic City, Sept.* 18–23, 1949) is an indication of present views on the subject, and includes some applications of Dr G. M. Dyson's cypher index, although I, for one, would hate to reduce hydrocarbon names down to a collection of apparently disjointed figures and letters. I make this point of nomenclature because of the possibility of the same compound receiving more than one name at the moment and confusing investigations in this particular field.

Secondly, I was interested in Dr Hickinbottom's example of a very high-melting-point hydrocarbon, since, in a paper by Dr Howes and myself, presented to the 11th International Congress of Pure and Applied Chemistry, it was pointed out that the first substitution in a normal paraffin chain depressed the melting point; a second substitution resulted in a further reduction, but eventually as the symmetrical molecule was approached, the melting point rose and ultimately was very high indeed. I cannot help thinking that what we look upon as a normal paraffin, in paraffin wax, may not necessarily be the straight-chain compound.

Finally, is it possible that in the next few years we shall also have similar data for sulphur compounds as for hydrocarbons? The Americans have commenced work on that problem, and is a most important step. I realize the difficulties, even in the case of hydrocarbons, since there are 355 possible paraffins of formula $C_{12}H_{26}$ and over 10,000 of formula $C_{16}H_{34}$. The more people who devote their abilities to this kind of work, the more information we shall have, and in such work, synthesis, analysis, and spectroscopic methods must all play their part.

D. G. JONES: A point which may be mentioned as an addendum to Mr. Lowry's paper is that of purity. I do not know what the Bureau of Standards do, but I was reading some of their work in which they found a quite stable hydroperoxide formed in the hydrocarbons. Presumably, if we want to repeat somebody else's work on what was a pure sample, we must have a purification stage before we can carry on further.

D. H. PEEL: I should like to know whether much progress has been made or is likely to be made in the direction of producing a larger number of hydrocarbons, and whether greater efforts are being made to purify them. Are we doing anything to correlate the physical properties with structure, so that we can get some order into this matter, and so that we can use such data to forecast the properties of unknown compounds?

THE CHAIRMAN: A symposium is to be held next session, I believe, at which I hope the Spectroscopic Group will deal with the correlation of spectra and structure; it will follow from the work discussed in September 1949 issue of the *Journal of the Institute* and from the work discussed this evening.

DR FIDLER: The question of correlating the physical properties of hydrocarbons, such as density, refractive index, and boiling point, with structure is a most interesting and important one. By interpolation from the relationships established with known hydrocarbons, it is often possible to predict the properties of hydrocarbons which are not readily available. A considerable number of papers dealing with this subject have appeared in the last few years.

THE CHAIRMAN: An important point which speakers have made this evening, I think, is that at the moment the values we have for hydrocarbons are few and the syntheses are difficult, and that it is essential, before trying to correlate physical properties with structure, to be absolutely certain that the product in respect of which you are evaluating the physical constants has the structure that you think it has. Much of the material which has appeared in the literature is not suitable for correlation. But I believe the work of our Synthesis Panel is of a high order, and we hope that it will lead to correlation.

DR D. P. YOUNG: I should like to ask Dr Porter how he makes his zinc dialkyls.

DR PORTER: You will find an exact account of our method in the *Journal* in the paper by Buck, Elsner, Forbes, Morrell, Smith, and Wallsgrove (*J. Inst. Petrol.*, 1948, **34**, 339–69).

D. H. PEEL: At one time I got into the habit of attempting to identify organic chemicals by their smell. The smell of compounds is perhaps not a physical property as such, but smell is very often due to impurities. We are now preparing compounds which are extremely pure, and it seems that there may be a theory which relates smell and structure. There may also

be some interest in recording the smell of the various compounds which have been prepared.

PROFESSOR TURNER: Would it not be necessary first to produce a standard nose?

THE CHAIRMAN: It is a point of interest. Do some of the pure hydrocarbons have a distinctive smell?

PROFESSOR TURNER: Almost all of them have characteristic smells, usually depending upon the shape of the molecule. Tertiary, butyl, or gem-dimethyl groups frequently give rise to a peppermint smell.

DR FIDLER: There is undoubtedly some correlation between smell and structure in the case of aromatic hydrocarbons. For instance, with this class of hydrocarbons, the smells produced by *ortho-*, *meta-*, and *para-* groupings are quite distinct and different.

K. VAN NES: There is a common feeling among people concerned with the constitution of mineral oils, that in the higher fractions *iso*paraffins are lacking. Although the study of the synthesis of higher *iso*paraffins is very interesting from a scientific point of view and may be important for the development of synthetic oils, it is questionable whether knowledge of *iso*paraffins provides information on petroleum products. It may be pointed out here that there are various groups of hydrocarbons present in petroleum, of which only very small numbers of representatives have been synthesized; for instance, molecules containing aromatic rings, naphthene rings, and paraffinic side chains side by side.

With regard to the correlation of the physical constants of hydrocarbons and their structure I invite attention to the study of J. Smittenberg (J. Smittenberg and D. Mulder, *Rec. Trav. chim.* 1948, **67**, 813–25, 826–38; 1949, **68**). This investigation succeeded in deriving formulæ for density and refractive index of various homologous series of hydrocarbons. With the aid of these relations physical properties of unknown compounds may be predicted with an accuracy similar to the accuracy of the data on synthesized members of the series.

VOTE OF THANKS.

THE CHAIRMAN: It is my pleasant duty to thank on your behalf Dr Fidler, Dr Porter, Dr Hickinbottom, Professor Turner, and their colleagues, and also to express the thanks of the Institute to the sponsoring bodies—the Ministry of Supply, Imperial Chemical Industries (Billingham) Ltd., the Anglo-Iranian Oil Co. Ltd., the Anglo-American Oil Co. Ltd., Trinidad Leaseholds Ltd., the Shell Petroleum Co. Ltd., and the Manchester Oil Refinery Ltd. We should express our thanks warmly to those bodies, whose support of the programme has made the work possible, and our friends who have contributed the papers for their presentation of a very very difficult subject.

(The vote of thanks was accorded with acclamation.)

DETERMINATION OF SATURATED AND AROMATIC CONSTITUENTS IN SPINDLE DISTILLATES AND DERIVED PRODUCTS BY ADSORPTION FRACTIONATION.

By G. H. Beaven, L. F. Foster,* and C. N. Thompson (Assoc. Fellow).

Summary.

A method has been developed for the quantitative separation, on an analytical or a preparative scale, of the aromatic and saturated compounds in petroleum products in the spindle-oil viscosity range, irrespective of the amounts present. The separation of an oil into saturated and aromatic fractions is based on the relative adsorptive affinities of the oil components for activated silica gel. The method is of particular value in exploratory work when little is known about the relative proportions and properties of these two main groups of constituents; it has found satisfactory application in the analysis of low-aromaticity oils for which other methods are less suitable.

By using a number of different eluants, the aromatic fraction may be fractionated further, and the results quoted indicate that there may be some segregation into mono-, di-, tri-, and poly-cyclic aromatics.

Introduction.

The method described in this paper was developed in the course of analytical studies of gas oils in the Thornton Research Centre,[1] and later with some modifications and standardization of technique, of transformer oils and related petroleum fractions. Its principal applications are :—

(a) *Measurement of the "aromatic content" of highly refined transformer oils, for which specific dispersion and ring analysis methods are insufficiently discriminating at the low levels of aromaticity encountered.*

(b) *As a preliminary to the separation of the aromatic and saturate constituents of petroleum fractions in the spindle-oil range on a* preparative *scale, using essentially the present technique but with simplifications based on the results of the analytical-scale separation. This use of the method is also discussed in the present paper.*

A brief survey of the applications of adsorptive percolation to the analysis of hydrocarbon mixtures has been given by Smit.[2a] During a discussion of Smit's paper at the International Congress on Analytical Chemistry (Utrecht, June 1–3, 1948), an outline of the work described in the present paper was contributed.[2b] Other recently published methods for the analysis of shale-oil naphthas [3] and high-boiling petroleum fractions [4] involve fractionation into non-aromatic and aromatic portions on the basis of the refractive index of the percolating material. The use of this criterion (refractive index) as the sole basis for deciding where the transition between saturates and aromatics occurs may give rise to errors; from the physical

* "Shell" Refining & Marketing Co. Ltd., Thornton Research Centre.

properties of pure hydrocarbons tabulated in the literature [5, 6] it is known that :—

(a) *Saturates exist with refractive indices* above *the limit usually encountered in work on light lubricating oil fractions* (e.g., 1·48) :—

1 : 3-*dicyclohexylcyclohexane*	n_D^{20} 1·494
cis-decalin	n_D^{20} 1·4811
9-n-*butylperhydroanthracene*	n_D^{20} 1·5049

(b) *Aromatics exist with refractive indices* below *the customary limit limit* (e.g., 1·49) *for the aromatic fractions of the same oils, and sometimes, even, within the nominal saturate limit :—*

e.g., 1-*phenyloctadecane*	n_D^{20} 1·481
1-*phenyldodecane*	n_D^{17} 1·474

The adsorptive affinities (for silica gel) of such hydrocarbons would be expected to depend on their structures regardless of their refractive indices. It would therefore seem more logical to base an adsorption fractionation on the relative adsorptive affinities for silica gel of the percolated oil fractions, rather than on the refractive indices. It has been found experimentally that the practical transition point between saturates and aromatics may be taken as occurring when the oil content of the percolate falls to a specified minimum value. At or near this point the refractive index n_D^{25} of the percolate oil fractions increases suddenly from about 1·47 to 1·50.

In oils containing a relatively high percentage of compounds of the types described above, a fractionation based on changes in refractive index during percolation may be in error. Nevertheless, it has been found that, in general, an analysis on the present basis is normally in good agreement with that made on the basis of refractive index measurements alone. Indeed, it is frequently of value to compare the results obtained by both criteria; for products from a given crude, the average refractive indices of, for example, the total saturates fall within sufficiently close limits in any given viscosity range to be of practical value in adsorption separations.

The present method of conducting the separation of saturates and aromatics is of particular value in exploratory work when very little is known about the relative proportions of these two main groups of constituents and their refractive indices and other physical and chemical properties. By using a large number of boiling tubes to collect small volumes of percolate and a solvent evaporator (described below) for the rapid removal of solvent, small fractions can be isolated and characterized during the actual course of the percolation, and can be bulked in any desired way as soon as the saturates/aromatics separation point has been decided. In subsequent experiments on the same sample, the cumulative percolated oil weights indicate when the previously established transition points are being approached, as also do the refractive indices.

Analytical Separation: Method.

Scope of the Method.

The method described below is applicable to all petroleum fractions in the spindle-oil viscosity range (and probably higher) irrespective of the

aromatic content of the oil. The separation of an oil into a saturated fraction and an aromatic fraction is based on the relative adsorptive affinities of the oil components for activated silica gel. It is not intended for use with compounded lubricants or additive-type products, unless it has been established that such non-hydrocarbon components do not interfere with the analytical separation.

Definitions.

(a) *Aromatic content* (per cent by weight). This is the percentage by weight of all oil constituents containing aromatic rings. Any saturated structures, such as paraffinic or naphthenic side-chains, or naphthenic rings fused to aromatic rings are included in the aromatic content. The figure also includes any polar constituents of the oil, such as sulphur, oxygen, and nitrogen compounds, which are adsorbed on silica gel at least as strongly as the oil aromatics.

This definition should not be confused with the "aromaticity," as determined by ring-analysis methods,[7, 8, 9] which is generally defined as "the percentage of carbon atoms in aromatic rings" or "the ratio of the number of carbon atoms in aromatic rings to the total number of carbon atoms in the average oil molecule." The "aromaticity," so defined, does not include saturated structures linked or fused to aromatic rings.

(b) *Saturates Content* (per cent by weight). This is the percentage by weight of hydrocarbons not containing aromatic rings, and includes paraffins, naphthenes, and mixed paraffin-naphthenes. Unadsorbed olefins which do not polymerize or isomerize in the presence of silica gel to adsorbable compounds may also be included in this figure.

Summary of the Method.

The oil sample, diluted with a suitable solvent, is separated into two main fractions: (i) saturates; (ii) aromatics; by adsorptive percolation through, and elution from, silica gel contained in a column of specified dimensions. Such experimental variables as silica gel/oil sample ratio, solvent volumes, etc., are standardized.

Apparatus.

(a) *Adsorption column* (See Fig. 1 (*a*)). This is a glass tube (30 in long × 1 in dia), fitted with a fine-porosity, sintered glass plate, a tap, and having at its upper end a bulb of approximately 250 ml capacity.

(b) *Abbe refractometer*, of standard type; this instrument should be capable of giving refractive indices accurate to within about ± 0·0002 for samples of small size (1–2 drops only).

(c) *Water-pump*, capable of producing a vacuum of 20 mm mercury or less. A cold-trap (solid CO_2–alcohol) of suitable dimensions should be inserted between the water-pump and the vessel containing the oil plus solvent.

(d) *High-vacuum oil-pump*, capable of producing a vacuum of 1–2 mm mercury or less. A similar cold trap is necessary.

(e) *Graduated measuring cylinders*: 2 of 25-ml and 1 of 50-ml capacity.

Either (f) *Flasks*, twelve 100-ml round-bottomed flasks with standard ground glass necks, and provision for connecting to vacuum,

and (g) *Air-leaks*, ground-glass joint to fit flasks (f),

or (h) *Solvent evaporator* of type shown in Fig 1 (*b*) and 5, together with at least a dozen boiling-tubes (graduated for 10 ml volume of liquid) of such dimensions that they will easily fit inside the steam-coil of the evaporator.

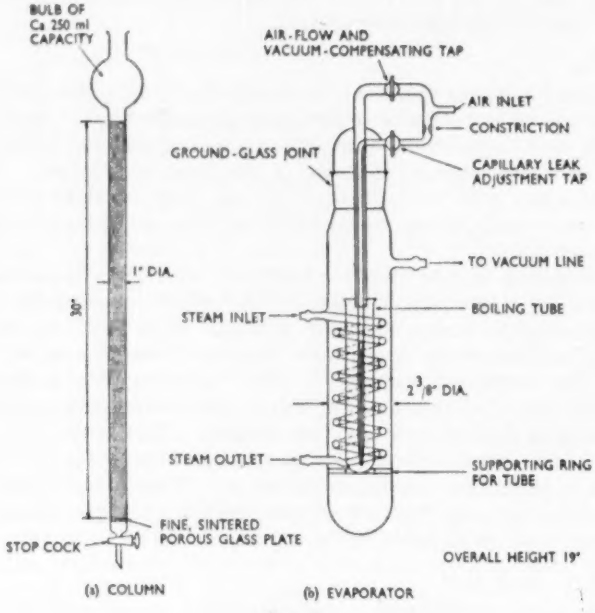

FIG. 1.

ADSORPTION FRACTIONATION EQUIPMENT.

Reagents.

(a) *Silica gel*, approximately 100–200 mesh size, activated prior to use in an oven at 150° C (± 10° C) for a period of 2 hr. The gel should be spread on a shallow tray for the activation process and allowed to cool in a suitable vessel (*e.g.*, a large evaporating dish) placed in a desiccator, which should not contain any desiccant.

(b) iso*Pentane or* 40–60° *C petroleum spirit.* The commercial product may be used, providing that it contains no hydrocarbons of boiling point greater than 60° C. Such redistilled solvents should contain negligible proportions of aromatics which would otherwise interfere with the efficiency of the fractionation.

(c) *Diethyl ether*, redistilled before use.

Procedure.

Into the adsorption column is weighed 120 g (± 5 g) silica gel, treated as above immediately prior to use. (The stop-cock at the base of the column should not be lubricated, but left dry.) Whilst placing the gel into the column, the latter should be ' bounced ' on the bench to assist uniform packing of the gel. A rubber stopper, partly bored with a hole of the

required diameter, and placed on the outlet at the base of the column will minimize the risk of breakage. A uniform packing of the gel reduces ' channelling ' of the percolating oil, which might result in an inaccurate analysis.

About 18 to 22 g oil is weighed out to the nearest 0·02 g, diluted with an approximately equal volume of *iso*pentane, and poured into the top of the column. The containing vessel is washed with the same solvent, and the washings are added to the column. Fresh *iso*pentane should be added to the column as required so that there is always a small volume of solvent above the gel.

The first 50 ml of percolate is collected as a single fraction which will contain a large proportion of the total saturates in the sample. From this point onwards, the percolate is collected in successive 10-ml ($\pm$ 0·5 ml) fractions.

The fractions are transferred from the graduated cylinder in which they are collected to flasks (or the fractions may be collected directly into graduated boiling-tubes if a solvent evaporator of the type indicated is used). The solvent is removed until each oil fraction attains constant weight, first using a water pump, and finally the high-vacuum oil pump for a short period to remove the last traces by either of two methods :—

(1) *Flasks* : These should be fitted with a ground-glass air-leak reaching to near the base of the flask, and also with a distillation head whose side-arm can be connected to the vacuum line. The flask containing the percolate fraction should be immersed in a beaker of warm water to minimize cooling whilst the solvent is being removed under vacuum.

(2) *Boiling Tubes* : a diagram of the solvent evaporator is given in Fig. 1 (*b*). The boiling-tube containing the percolate fraction is inserted into the evaporator, being placed inside the steam coil by means of a wire loop which may be attached temporarily for the purpose to a wire hook on the tube. (The latter is also of use during weighings.) A water-pump vacuum line is attached to the evaporator in the position shown after the tap system (with taps open) has been placed in position. Apply vacuum cautiously, adjusting both taps so that : (i) the capillary air-flow is at a moderate rate, sufficient to promote steady ebullition but not so vigorous as to cause the sample to froth over ; (ii) the upper tap is adjusted so that, (*a*) solvent vapours are flushed readily down the pump line, and (*b*) any frothing tendency is minimized.

Successive 10-ml fractions of the percolate should be collected and treated in the same manner until the oil contents of two consecutive fractions are less than 0·2 g. The point where this occurs depends on the saturates content of the oil, and also on the slight adsorptive affinity of the silica gel for the saturates. Fig. 2 illustrates the rapid decrease in oil content of successive percolate fractions. As it is generally impracticable to strip the solvent from each percolate fraction before the next has been collected it is advisable to collect five successive 10-ml fractions, and then close the stopcock at the base of the column whilst working up these fractions. Weigh each oil fraction, and determine its refractive index. The refractive index

may not be determinable for fractions in the transition region between saturates and aromatics where oil contents are very small.

If the oil content of two successive fractions is not less than 0·2 g each, then further 10-ml samples should be taken and worked up separately until this is the case.

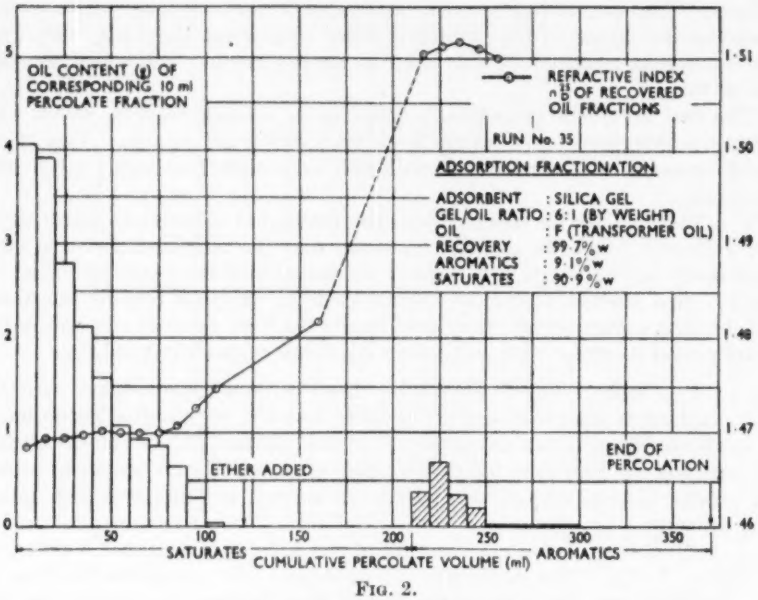

FIG. 2.

ADSORPTION FRACTIONATION.

If, however, the oil present in successive 10-ml fractions :—

(i) remains constant in amount at a weight greater than 0·2 g, or
(ii) increases in amount without having decreased below 0·2 g, or
(iii) becomes coloured or fluorescent (or both), then it is probable that—

(*a*) the silica gel was not packed evenly in the column, in which case the fractionation should be repeated using a more vigorous packing technique, or

(*b*) the gel/oil ratio was too small to permit an efficient separation.

The latter contingency (*b*) is unlikely unless the silica gel is of low activity, or the sample has a very high content of aromatics. In such cases, a higher gel/oil ratio (*e.g.*, 10 : 1 or 15 : 1 by weight) should be used and 10-ml fractions collected from the start of the percolation, working these up separately. The variation in oil content and refractive index of these initial fractions may later prove a valuable guide if the oil is of high aromatic content.

When the oil content of successive equal percolate volume fractions reaches the small value referred to above, redistilled diethyl ether is added to the top of the column. (From this point until the end of the percolation, addition of ether is necessary from time to time so that a small volume always remains above the gel.) Immediately after the first addition of ether at the top, the stop-cock should be removed and washed in the stream of percolating solvent. The barrel of the tap should also be washed with a little *iso*pentane, and all the washings collected. The stop-cock is now replaced and the percolation allowed to proceed, receivers being changed when the washings plus percolate reach the 50-ml graduation mark. This solvent is worked up as before, any residual oil is weighed, and its refractive index is determined. A further 50 ml of percolate is collected and worked up similarly. By this time the coloured band of aromatics will be near the base of the column, and therefore separate 10-ml fractions should now be collected until the last of the dark band has been collected. This is best checked by working up successive fractions until their oil content is negligible (that is, less than 0·05 g). These fractions should be worked up as before, weighed, and their refractive indices determined whenever possible.

Calculation and Reporting.

The following values are plotted graphically :—

(i) Oil content (g) of equal volumes of percolating solvent against the cumulative percolate volume, using the block-diagram method as in Fig. 2.

(ii) Refractive index (n_D^{25}) of oil fractions against the mean of the percolate volume from which the fraction in question was obtained.

" Saturates " are regarded as all the oil fractions up to and including the one having the smallest weight before the aromatics emerge from the column. This occurs at a cumulative percolate volume of 210 ml for the fractionation of oil F (Fig. 2), but this volume varies according to the aromatic content of the oil and the degree of polarity of the oil components. Usually, the transition point between aromatics and saturates is easily discernible, since :—

(*a*) the weight of oil per unit volume decreases rapidly, remains at a low figure, and then increases steadily; and

(*b*) the refractive index (n_D^{25}) of the oil fractions increases suddenly to a value in the region of 1·50 to 1·51.

" Aromatics " are regarded as all the oil fractions which are obtained after this transition point. The weights of all the saturate fractions are added together and also those of the aromatic fractions. The two totals are added to give a combined weight of recovered oil. If the recovery is less than 98 per cent or greater than 102 per cent the fractionation should be repeated. If the recovery is consistently greater than 102 per cent, it is probable that some or all of the fractions contain unremoved solvent. In such cases, a longer vacuum treatment should be used.

It is convenient to report the results in percentages as follows :—

$$\text{Aromatics (per cent weight)} = \frac{A}{R} \times 100$$

$$\text{Saturates (per cent weight)} = \frac{S}{R} \times 100$$

$$\text{Recovery (per cent weight)} = \frac{R}{W} = \frac{A + S}{W}$$

where A = weight (in g) of the combined aromatic fractions,
R = total weight (in g) of oil recovered,
S = weight (in g) of the combined saturate fractions,
W = weight (in g) of oil used for fractionation.

TABLE I.

Adsorption Fractionation Analysis.

Oil : F Gel/oil ratio : 6 : 1 Wt of oil charge : 20·40 g.

Fraction.	Volume, ml.	Cumulative volume, ml.	Wt of Oil, g.	Cumulative wt, g.	Eluant.	Refractive index, n_D^{25}.	Remarks.
1	10	10	4·05	4·05	*iso*Pentane	1·4684	Fractions 1–12
2	10	20	3·93	7·98	,,	1·4694	inclusive are
3	10	30	2·80	10·78	,,	1·4694	colourless, non-
4	10	40	2·13	12·91	,,	1·4698	fluorescent sat-
5	10	50	1·58	14·49	,,	1·4702	urates.
6	10	60	1·08	15·57	,,	1·4700	
7	10	70	0·94	16·51	,,	1·4700	
8	10	80	0·86	17·37	,,	1·4700	
9	10	90	0·65	18·02	,,	1·4707	
10	10	100	0·32	18·34	,,	1·4728	
11*	10	110	0·05*	18·39	,,	1·4748*	Ether added at
12*	100	210	0·10*	18·49	,,	1·4821*	120 ml.
13	10	220	0·40	18·89	Ether	1·5108	Fractions 13–18
14	10	230	0·72	19·61	,,	1·5120	inclusive are
15	10	240	0·38	19·99	,,	1·5128	yellow, fluores-
16	10	250	0·24	20·23	,,	1·5118	cent aromatics.
17	50	300	0·09	20·32	,,	1·5102	
18	70	370	0·02	20·34	,,	—	Viscous yellow oil.

* It was apparent that after Fraction 11 had been collected the oil content of the next fractions would be too small to permit refractive-index measurements. Consequently, the next ten 10-ml fractions were bulked and called "fraction 12." It is probable that this small fraction contains admixed saturates and aromatics, but in view of its refractive index, the majority of the components present are presumably of a saturated type, and the remainder hybrid types. The transition point is therefore regarded as effectively between Fraction 12 and Fraction 13.

Percentages by weight:

$$\text{Aromatics} = \frac{1{\cdot}85}{20{\cdot}34} = 9{\cdot}1$$

$$\text{Saturates} = \frac{18{\cdot}49}{20{\cdot}34} = 90{\cdot}9$$

$$\text{Recovery} = \frac{20{\cdot}34}{20{\cdot}40} = 99{\cdot}7$$

Precision and Accuracy.

The percentages of aromatics or saturates should not differ by more than ± 2 per cent by weight from the mean result. It has usually been found that, for highly refined oils at least, duplicate analyses rarely differ by more than 0·5 per cent by weight for the aromatics or saturates content.

The total recovery should not be less than 98 per cent by weight nor more than 102 per cent. The difference between the recovery and 100 per cent is an approximate indication of the maximum possible error in the weight percentages of either the saturates or the aromatics.

Discussion of Results.

The results of a typical adsorption fractionation using the above method are given below (Table I). Initially, separate 10-ml fractions of percolate were taken.

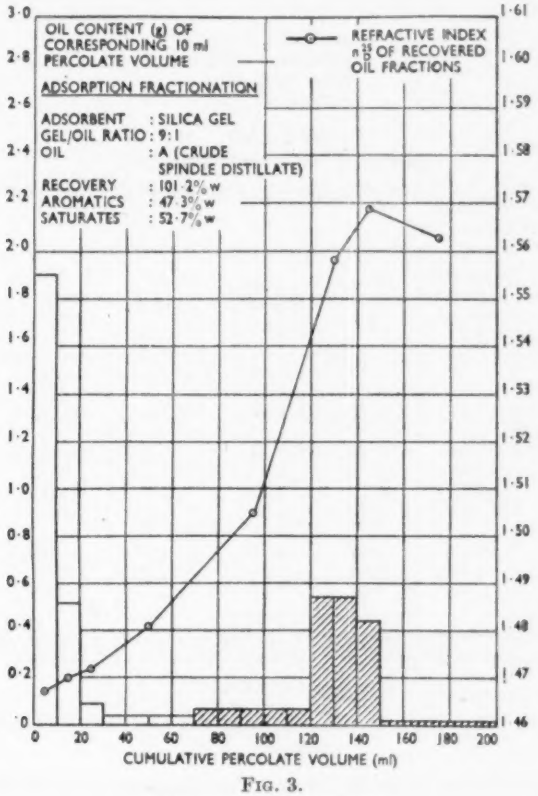

Fig. 3.

ADSORPTION FRACTIONATION.

Further typical examples of adsorption fractionation analyses, carried out while the above method was being standardized are given below. The results in Table II and Fig. 3 refer to a fractionation of a crude spindle

TABLE II.

Adsorption Fractionation Analysis.

Oil : A (Crude spindle distillate)
Gel/oil ratio : 9:1
Wt of oil charge : 5·00 g.

Fraction.	Volume, ml.	Cumulative vol., ml.	Wt of oil, g.	Cumulative wt, g.	Eluant.	Refractive index, n_D^{25}.	Remarks.
1	10	10	1·89	1·89	*iso*Pentane	1·4670	Colourless
2	10	20	0·52	2·41	,,	1·4698	,,
3	10	30	0·09	2·50	,,	1·4718	,,
4	40	70	0·17	2·67	,,	1·4807	,,
5	50	120	0·35	3·02	Ether	1·5049	Yellow
6	20	140	1·08	4·10	,,	1·5580	,,
7	10	150	0·87	4·97	,,	1·5688	,,
8	50	200	0·09	5·06	,,	1·5625	,,

Per cent by weight
Recovery 101·2
Aromatics 47·3
Saturates 52·7

TABLE III.

Adsorption Fractionation Analysis.

Oil : C (Edeleanu aromatic extract from a crude spindle distillate).
Gel/oil ratio : 9:1
Wt of oil charge : 5·20 g

Fraction.	Volume, ml.	Cumulative volume, ml.	Wt of oil, g.	Cumulative wt, g.	Eluant.	Refractive index, n_D^{25}.	Remarks.
1	5	5	0·32	0·32	*iso*Pentane	1·4690	Colourless
2	5	10	0·17	0·49	,,	1·4725	,,
3	50*	60	1·11	1·60	Ether	1·5135	Yellow, fluorescent
4	20	80	0·44	2·04	,,	1·5364	,,
5	20	100	0·33	2·37	,,	1·5499	,,
6	13	113	0·17	2·54	,,	1·5614	,,
7	10	123	1·22	3·76	,,	1·5903	Brown, fluorescent
8	10	133	0·97	4·73	,,	1·5950	,,
9	10	143	0·34	5·07	,,	1·6004	,,
10	50	193	0·08	5·15	,,	1·5868	,,

* The third 5-ml fraction contained a negligible amount of oil, so this was bulked with the subsequent 45-ml percolate and ether was added at this point.

Per cent by weight
Recovery 99·0
Aromatics 90·5
Saturates 9·5

distillate, whilst those in Table III and Fig. 4 refer to an Edeleanu aromatic extract of this oil. Experience has shown that the transition point between saturates and aromatics becomes rather less determinate at a constant gel/oil ratio as the aromatic content increases. This is seen to be particularly the case in Fig. 4 (aromatic extract analysis) where the refractive index of the fractions in the transition region proved to be an invaluable

guide. It is probable that the use of a more highly activated silica gel, or of a higher gel/oil ratio would in such cases give a more clear-cut separation of hydrocarbon types.

The analyses of some other products to which this method has been applied are given in Table IV.

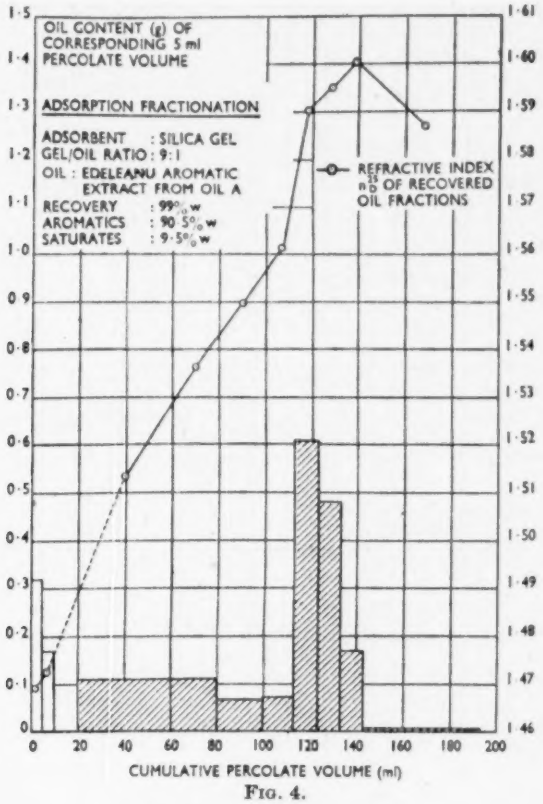
OIL CONTENT (g) OF CORRESPONDING 5 ml PERCOLATE VOLUME
ADSORPTION FRACTIONATION
ADSORBENT : SILICA GEL
GEL/OIL RATIO : 9:1
OIL : EDELEANU AROMATIC EXTRACT FROM OIL A
RECOVERY : 99% w
AROMATICS : 90·5% w
SATURATES : 9·5% w
REFRACTIVE INDEX n_D^{25} OF RECOVERED OIL FRACTIONS
CUMULATIVE PERCOLATE VOLUME (ml)

FIG. 4.

ADSORPTION FRACTIONATION.

TABLE IV.

Adsorption Fractionation Analyses for Various Products.

Ref. Letter.	Product.	Aromatics, % w.	Saturates, % w.	Recovery, % w.
A	Crude spindle distillate . .	47·3	52·7	101·2
B	Spindle oil	47·1	52·9	100·3
C	Edeleanu aromatic extract .	90·5	9·5	99·0
D	,, raffinate . . .	6·8	93·2	99·9
E	Solvent refined, acid-treated transformer oil . . .	4·7	95·3	100·5
F	Transformer oil similar to E .	9·1	90·9	99·7
G	Technical white oil . . .	1·2	98·8	99·4
H	Synthetic oil	84·8	15·2	98·6

Preparative Scale Fractionations into Two Components.

In order to prepare fractions of some of the products referred to above on a scale large enough for further analytical and research work, columns containing 600 g. of silica gel (or more) were used. Duplicate analyses of

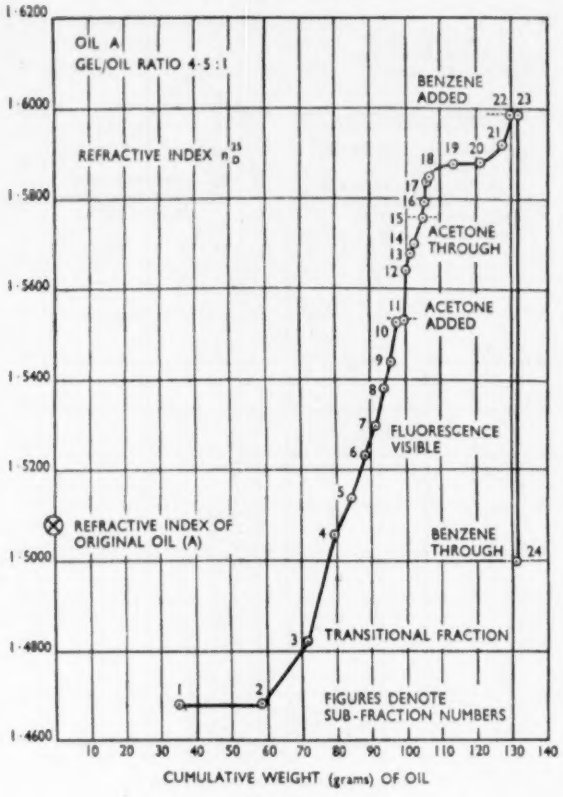

Fig. 6.

PREPARATIVE SCALE ADSORPTION FRACTIONATION.

oil A gave a recovery of 99·7 per cent by weight (aromatic content in each analysis was 49·2 per cent by weight) and provided approximately 70 g of each fraction for further studies. Further fractionations, under the same conditions, with the object of preparing the saturates (white oil) fraction of this oil, gave results which were in substantial agreement with those above (per cent by weight saturates: 50·1, 50·9, 51·6, 50·8, 51·1; average 50·85). In a similar manner, small samples (1 to 2 g) of the aromatic fractions from a technical white oil were obtained from a number of fractionations carried out using about 100 g oil charge (gel/oil ratio 6:1). The aromatic fractions were pale yellow in colour, of refractive index (n_D^{25}) in the region of 1·50 to 1·51. The low aromaticity of the saturates from the technical white oil was confirmed by ultra-violet spectroscopic measurements. As judged by

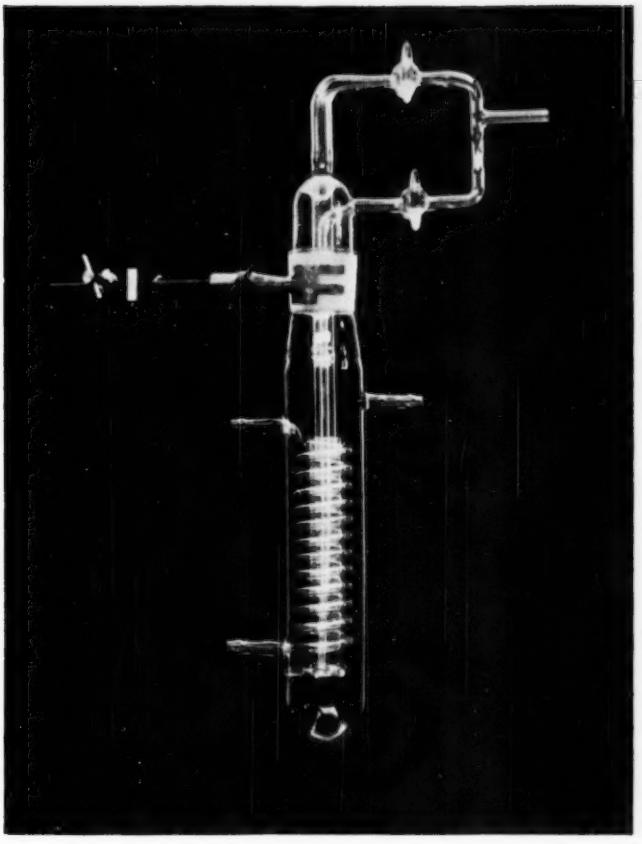

FIG. 5.

SOLVENT EVAPORATOR FOR RAPID PREPARATION OF FRACTIONS FROM ADSORPTION ANALYSES.

[*To face p.* 100.

the extinction coefficient at 2730 Å (viz., $E^{1\%}_{1\ cm.}$ of *ca* 0·0045) this corresponded to approximately 0·025 per cent by weight adsorbable aromatics.

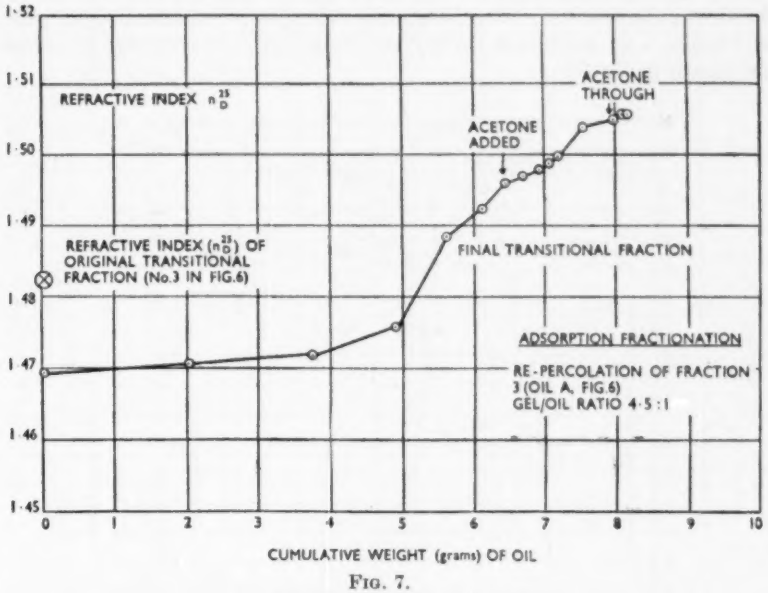

FIG. 7.

ADSORPTION FRACTIONATION.

During the development of this preparative scale work, oil A was percolated in solution in *iso*pentane through a 600-g silica-gel column (gel/oil ratio 4·5 : 1). From the results obtained it was clear that the gel/oil ratio was not sufficiently high, as about 10 per cent by weight of the percolate oil (n_D^{25} 1·5079) was collected as a single fraction (n_D^{25} 1·4823) in the transitional region. For a clear-cut transition, this should have been less than 1 per cent by weight, as specified in the analytical section of the present paper. Part of this transitional fraction of doubtful composition was re-percolated, using the same gel/oil ratio. A similar percentage was again of doubtful composition (n_D^{25} 1·4885), but this portion amounted to only 0·8 per cent of the total. The final product analysis gave 50·2 per cent by weight saturates and 49·8 per cent aromatics. (See Fig. 6 and 7.)

PREPARATIVE SCALE PERCOLATIONS : MULTISOLVENT DESORPTION.

By using a succession of developing solvents (*i.e.*, eluants of increasing adsorptive affinity for silica gel), the aromatic fraction may be fractionated further. The following solvents were used, in order :—

1. (*a*) *iso*pentane
   (*b*) carbon tetrachloride
   (*c*) ether
   (*d*) acetone
   (*e*) benzene
2. (*a*) *iso*pentane
   (*b*) carbon tetrachloride
   (*c*) ether

Using five solvents it was found that the majority (*ca* 75 per cent) of the aromatics were desorbed by carbon tetrachloride and nearly 25 per cent by ether. Acetone and benzene desorbed only a further 0·3 and 0·15 per cent by weight respectively. The progressive changes in fraction weight, refractive index, and dispersion during the course of a five-solvent percolation are shown in Fig. 8.

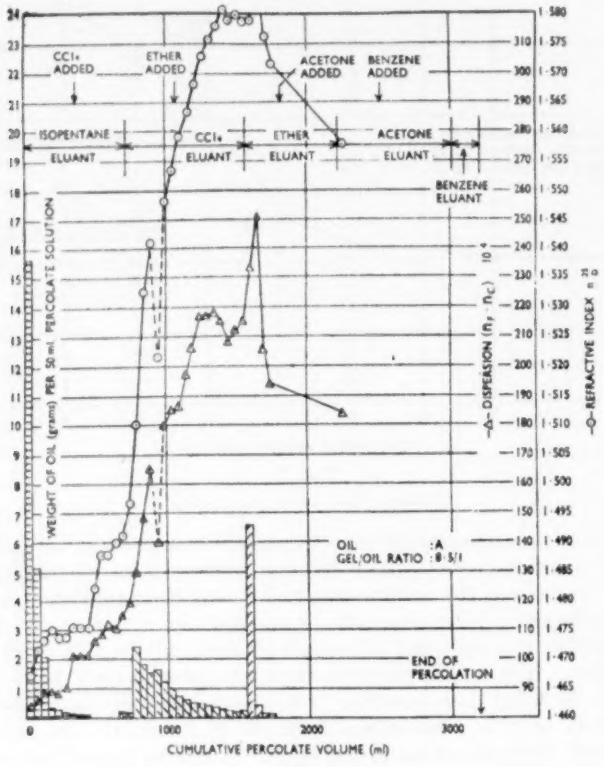

FIG. 8.

MULTI-SOLVENT DESORPTION ANALYSIS.

Using only *iso*pentane, carbon tetrachloride, and ether, three main fractions may be desorbed. The first consists of colourless, odourless, non-fluorescent saturates having a low refractive index (*e.g.*, 1·470) and zero sulphur content. The second fraction (eluted by carbon tetrachloride) is a yellow oil, the subfractions of which have a wide range of refractive indices and sulphur contents. The fraction desorbed by ether is a dark-brown oil, and the sub-fractions show similar trends. (See Fig. 9 for a typical fractionation.) The average results obtained during four three-component percolations of this type are given in Table V.

It is therefore clear that, although some segregation of aromatic types is possible by such methods, the sulphur compounds are found, under the

present conditions of analysis, to be distributed throughout the aromatic fractions. From the oil (A) examined, no entirely sulphur-free aromatic fraction was isolated. The changes in dispersion and refractive index which occur during continuous desorption indicate that there may be some segregation into mono-, di-, tri-, and poly-cyclic aromatics.

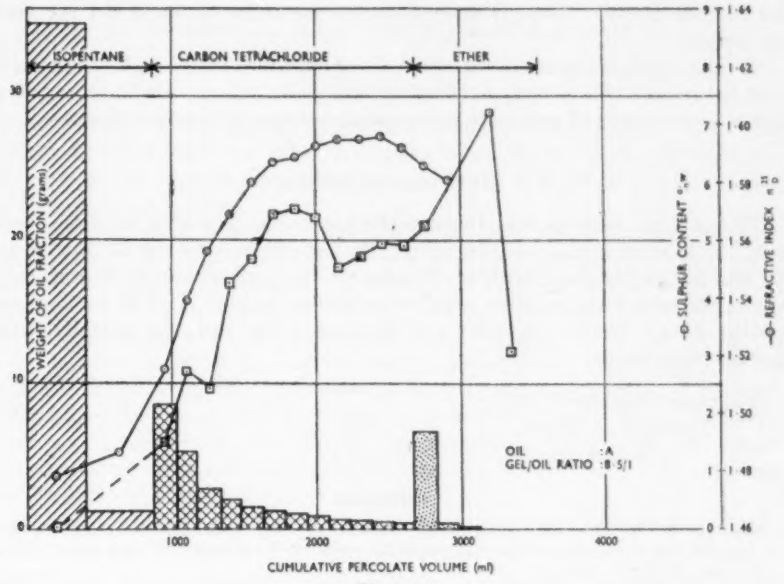

FIG. 9.

THREE-SOLVENT DESORPTION ANALYSIS.

TABLE V.

Preparative Scale Fractionations Using iso*Pentane, Carbon Tetrachloride, and Ether.*

Fraction.	Yield, % w of oil A.	Refractive index, n_D^{25}.	Dispersion, $(n_F - n_C) \times 10^4$.	Sulphur, % w.
Saturates	49·6	1·469	82–85	0·0
Transitional (saturates/aromatics)	3·7	1·469–1·495	87–121	—
Aromatics I *	35·5	1·546–1·554	174–182	1–5
Aromatics II †	10·9	1·581–1·587	217–335	ca 5
Average recovery, % w	99·7			

* Aromatics I desorbed by carbon tetrachloride.
† Aromatics II desorbed by ether.

CONCLUSIONS.

1. The method is applicable to any spindle-oil fraction irrespective of its aromatic content.

2. The aromatic content, defined here as the percentage by weight of compounds containing aromatic rings (but including also sulphur compounds and other polar constituents) is determinable with an accuracy of about $\pm$ 2 per cent or better.

3. The " saturate " fractions (paraffins, naphthenes, and mixed paraffin–naphthenes) and aromatic fractions may be recovered separately, if required for further study. Total recoveries are of the order of 99 to 101 per cent by weight.

4. The application of the method to preparative scale work is outlined, and the results of some experiments on this scale with a view to segregating the various types of aromatic compounds present in oils are discussed.

Acknowledgments.

The authors wish to acknowledge the assistance provided by discussions with A. J. Ham and J. G. Reynolds; thanks are due also to E. Mears and F. Wainwright of the Thornton Research Centre glassblowing department, who constructed the solvent evaporator shown in Fig. 5. The authors are indebted to " Shell " Refining and Marketing Co. Ltd., for permission to publish this paper.

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Thornton-le-Moors,
Chester, England.

References.

[1] Barclay, C. M., Bryant, S. A., and Backhouse, T., Thornton Research Centre, unpublished investigations, and paper in press by Backhouse, T. and Ham, A. J., *Fuel*, 1949, **28**, 246.
[2] (*a*) Smit, W. H. *Anal. Chim. Acta*, 1948, **2**, 671; (*b*) Beaven, G. H. *Anal. Chim. Acta.*, 1948, **2**, 679.
[3] Dinneen, G. U., Bailey, C. W., Smith, J. R., and Ball, John S. *Anal. Chem.*, 1947, **19**, 992.
[4] Lipkin, M. R., Hoffecker, W. A., Martin, C. C., Ledley, R. E. *Anal. Chem.*, 1948, **20**, 130.
[5] Gruse, W. A., and Stevens, D. R., " Chemical Technology of Petroleum," 1942 (Appendix).
[6] Schiessler, R. W., *et al.* *J. Amer. chem. Soc.*, 1948, **70**, 530.
[7] Vlugter, J. C., Waterman, H. I., and van Westen, H. A. *J. Inst. Petrol. Tech.*, 1932, **18**, 735.
[8] Vlugter, J. C., Waterman, H. I., and van Westen, H. A. *J. Inst. Petrol. Tech.*, 1935, **21**, 661.
[7] Deanesly, R. M., and Carleton, L. T. *Ind. Eng. Chem. Anal.*, 1942, **14**, 220.

POWER RIG REQUIREMENTS FOR DEEP DRILLING IN TRINIDAD.

By James S. Blair * and Richard J. Gaul.*

Introduction.

Since the war there has been a growing trend to seek oil production from depths below 10,000 ft. The result has been an increasing demand for manufacturers to design larger equipment that will be adequate for drilling to these greater depths.

Geological studies seem to indicate that deep-producing horizons are present in Trinidad, and the various companies are now actively engaged in drilling to these deeper structures, which it is believed will be encountered between 12,000 and 15,000 ft. Since drilling conditions in Trinidad are out of the ordinary in several respects, when compared with similar operations in other parts of the world, a very careful study of drilling requirements must be made by the drilling and equipment engineers. A decision must be reached as to whether steam or power equipment should be used, and as a large part of the local exploratory work will be done in remote areas, lacking adequate fuel and water for steam operations, the internal-combustion rig is often the only choice.

Although large power rigs have been developed and used in the U.S.A. during the last ten years, it is only within the latter eighteen months that this type of rig has been introduced to Trinidad for deep-drilling operations. Of the few wells drilled locally to below 10,000 ft, only two have been drilled with power rigs, and therefore operating and maintenance experience of this type of equipment is necessarily limited. For this reason local operators may find it a little difficult to select power equipment to properly handle their requirements for deep drilling.

While the basic function of both steam and power rigs is the same, the different characteristics of their respective power sources make it very difficult to form a true comparison. In addition, power-rig equipment is generally much heavier than the corresponding steam-operated machinery. The latter raises the problem of transportation over local roads and terrain, neither of which is particularly suited to the movement of heavy loads, which may weigh 30 tons, or more.

The following comments are based on discussions with local operators, and upon recently published technical papers, and it is hoped that they will present the salient points to be considered in the selection of a power rig for deep drilling in Trinidad.

All hydraulic calculations are based on the use of plain shale mud, or this same mud weighted with barytes. Although the use of oil-base and oil-emulsion muds in Trinidad has developed rapidly in recent months, it would still seem to be in the experimental stage, as applied locally, and rig-

* Neal and Massy Engineering Co. Ltd., Trinidad.

performance figures when using these muds, are not as yet generally available. There is reason to believe, however, that if the use of this type of mud becomes general in the Island, considerable modification will be necessary to both casing programme design and to anticipated pump-pressure calculations, which in turn will require changes in the rig-engine arrangement and other features.

Hydraulic Horsepower Requirement.

In order properly to discuss the major diesel rig requirements for 15,000-ft drilling in Trinidad, it should be borne in mind that, due to unusual geological features, subsurface pressures are often higher than generally encountered at equal depths elsewhere. The direct result of this is the need to carry heavy muds practically from the surface, and consequently the necessity to have pumping capacity adequate to handle these heavy muds. It has been found by local operators, that if they have sufficient hydraulic horsepower available to handle the necessary mud conditions, then there is ample power available for handling the drill pipe and casing ordinarily used in these wells. The rotary drive may be from an independent source, or it may be from the drawworks. In either case the power requirement is small, compared with that used in hoisting or pumping. Thus, the power requirement for a diesel rig to operate in Trinidad is governed to a large extent by the hydraulic horsepower requirements of the rig or well, rather than by the hoisting power necessary. The most economical rig would, of course, be the one in which the hydraulic horsepower exactly matched the hoisting horsepower at equal depths.

Casing Programme.

In order to arrive at some definite figures covering these local hydraulic horsepower requirements, it is proposed to assume a given casing and drill-pipe programme, discuss it briefly, and then calculate the various pressures and volumes required to be delivered by the mud pumps to the hydraulic system. The assumed casing programme is :—

Drill 24-*in hole and set* 20-*in* × 94-*lb casing at* 1000 *ft.*
Drill 17½-*in hole and set* 13⅜-*in casing at* 5000 *ft.*
Drill 12¼-*in hole and set* 9⅝-*in casing at* 10,000 *ft.*
Drill 8½-*in hole and set* 5½- *or* 5-*in casing at* 15,000 *ft.*

No weights or grades have been specified in the above casing sizes, since these will have to be fixed by a given set of conditions when an actual well is to be drilled. However, for easy reference, the setting depths and resulting safety factors are given in Table I for the probable weights and grades to be used, on the assumption of 72-lb mud for surface hole plus 100-, 110-, and 120-lb mud for the remainder, depending on depth. These figures are taken to be average local mud weights and give pressure gradients of approximately 0·70, 0·77, and 0·84 p.s.i/ft of depth, respectively, as compared with the figure of 0·5 p.s.i/ft of depth which is generally used in the various published tables of setting depths. As far as possible a safety factor of 1·125 will be used for collapse, and a factor of 1·8 for tension, these being accepted values based on the minimum yield point of the material used.

TABLE I.

Casing Setting Depths and Safety Factors.

Size, in.	Weight, lb/ft.	Grade.	Setting depth, ft.	Safety factors.		Remarks.
				Collapse.	Tension.	
20	94	H–40	920	1·125	Over 5	72-lb mud assumed for 1st 1000 ft.
13⅜	72	N–80	3040	1·125	Over 2 at 5000 ft.	120-lb mud.
,,	,,	,,	3430	1·00	,,	,,
,,	,,	,,	5000	0·685	,,	,,
,,	,,	,,	4100	1·125	,,	100-lb mud.
,,	,,	,,	5030	1·00	,,	,,
9⅝	53·5	N–80 Ex. Line	6480	1·125	Over 2 at 10,000 ft.	120-lb mud.
,,	,,	,,	7300	1·00	,,	,,
,,	,,	,,	10,000	0·73	,,	,,
,,	,,	,,	7100	1·125	,,	110-lb mud.
,,	,,	,,	8000	1·00	,,	,,
,,	,,	,,	10,000	0·8	,,	,,
,,	,,	,,	8800	1·00	,,	100-lb mud.
5½	23·00	,,	9400	1·125	1·54 at 15,000 ft.	120-lb mud.
,,	,,	,,	10,560	1·00	,,	,,
,,	,,	,,	15,000	0·7	,,	,,
,,	,,	,,	10,250	1·125	,,	110-lb mud.
,,	,,	,,	11,550	1·00	,,	,,
,,	,,	,,	15,000	0·77	,,	,,

Figures for 5-in casing are very similar to those for the 5½-in size given.

In Table I the heaviest and best grades of casing available in each size range have been taken, and it will be seen that if mud no heavier than 120 lb is used, there is no available 13⅜-in or smaller casing, that can be set at the proposed depths and still retain the accepted safety factors in collapse. In the event heavier muds are used these figures have to be modified again, resulting in a further reduction of the collapse safety factors. In short, there is no casing generally available that will stand up under the collapsing pressures that are commonly met in Trinidad deep drilling. The previous statement assumes that the casing is empty, in order that these extreme conditions should exist. In practice the casing is not empty as a general rule, but might become so, and it is then that the danger of collapse becomes apparent. When casing becomes generally available in S.A.E. 4340 material, having a minimum yield point at 105,000 p.s.i., then for plastic failure in collapse the tabulated figures could all be increased by about 32 per cent. This would improve the general picture and make 20,000 ft drilling in Trinidad a practical proposition (from the standpoint of having casing available when the hole is drilled), even though the collapse safety factors might not be all that could be desired.

The bursting strengths of the above casings are all of such value that a safety factor in the neighbourhood of 1·0 is attainable, with the exception that very heavy muds will reduce this to some lower figure. However, as in the case of the collapse strength, it is not generally anticipated that extreme bursting conditions will be encountered under ordinary circumstances.

Several long strings of $9\frac{5}{8}$-in casing have already been set in the U.S.A., utilizing standard casing and having a safety factor around 0·8 in collapse. It would seem that, if any deep wells are drilled in Trinidad in the near future, a similar practice will have to be adopted for want of better casing material.

Drill Pipe.

Turning now to the drill pipe to be used in the above suggested casing strings, several general factors influence the choice. Possibly the most important is the need to reduce the pressure drop through the drill pipe and tool joints, thus making available at the bit more energy in the form of pressure, that can be utilized in a jetting action to keep the bit clean and the cuttings broken up. In addition, a suitable return annular velocity is necessary, in order that the cuttings may be brought to the surface. In this connexion R. J. Piggot has shown that the maximum slip velocity of particles in an ascending stream of water is about 0·9 f.p.s. Taking this as a basis for calculations, and assuming that the slip velocity of cuttings in mud will not be greater than this (and probably much less), an annular velocity of 1·0 f.p.s. is taken as the minimum for purposes of this discussion.

If the largest size of drill pipe that will pass through the casing is used, the pressure drop down the pipe will be a minimum and the annular return velocity a maximum—both desirable features. However, reasonable clearance is needed between the tool joints and casing for successful operation, and to cover the possibility of having to run finishing tools over a stuck string of drill pipe. Therefore, a compromise must be made.

Drill pipe that is currently available consists of the following sizes :—

$5\frac{1}{2}$-in outside dia with 7-in outside dia full hole tool joints.
5-in outside dia with $6\frac{1}{8}$-in outside dia $4\frac{1}{2}$-in internal flush tool joints.
$4\frac{1}{2}$-in outside dia external upset with $6\frac{1}{8}$-in outside dia internal flush tool joints.
$4\frac{1}{2}$-in outside dia internal upset with $5\frac{3}{4}$-in (or 6-in) outside dia full hole tool joints.
4-in outside dia external upset with $5\frac{3}{4}$-in outside dia internal flush tool joints.

In addition, there is available a $4\frac{1}{2}$-in outside dia pipe with extra-hole tool joints, which consists of the 4-in internal flush joint attached to the $4\frac{1}{2}$-in pipe; there are also some smaller sizes of pipe, but local operators have found that for general drilling operations with heavy muds these are impracticable, due to excessive pressure drop resulting in low volume of mud and slow returns. In so far as the larger surface holes and casing are concerned, even the available sizes of drill pipe are really too small, since the pressure drop is relatively large for the necessary volume of mud that has to be pumped to obtain an annular return velocity of 1·0 f.p.s. However, the larger sizes of drill pipe which used to be available, while being more suitable from the hydraulic standpoint, were unwieldy to handle and, more important, were too rigid for satisfactory use at any but relatively shallow depths. Again, lacking exactly suitable material, the best solution would probably be the current $5\frac{1}{2}$-in outside dia drill pipe with 7-in outside dia full-hole tool joints, for all drilling down to 10,000 ft. Reference to Figs. 1–9 will indicate the pressure drops that can be expected with this size of pipe whilst circulating various volumes of mud.

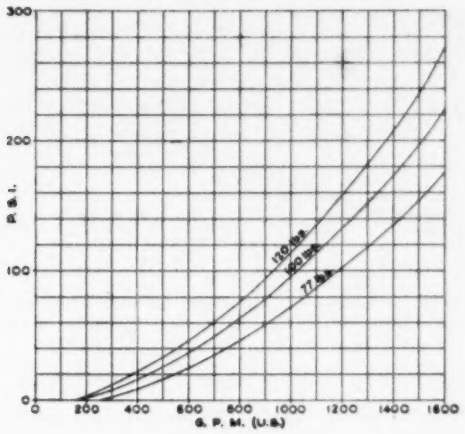

FIG. 1.

DRILL-SIZE PRESSURE LOSSES IN RELATION TO MUD WEIGHT AND FLOW—$6\frac{5}{8}$-IN O.D. WITH $7\frac{3}{4}$-IN REGULAR TOOL JOINTS.

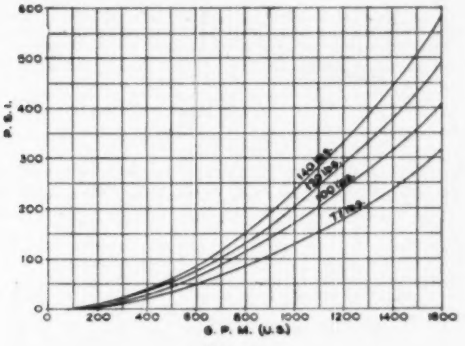

FIG. 2.

DRILL-PIPE PRESSURE LOSSES IN RELATION TO MUD WEIGHT AND FLOW—$5\frac{1}{2}$-IN O.D. WITH 7-IN O.D. FULL HOLE TOOL JOINTS.

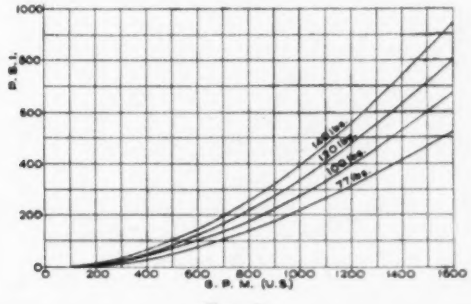

FIG. 3.

DRILL-PIPE PRESSURE LOSSES IN RELATION TO MUD WEIGHT AND FLOW—5-IN O.D. WITH $6\frac{1}{2}$-IN O.D. INTERNAL FLUSH TOOL JOINTS.

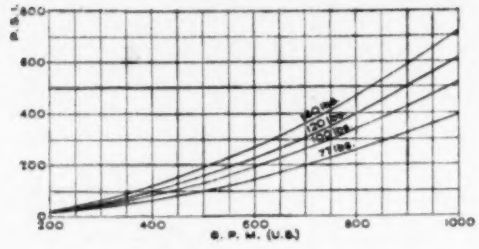

FIG. 4.

DRILL-PIPE PRESSURE LOSSES IN RELATION TO MUD WEIGHT AND FLOW—$4\frac{1}{2}$-IN O.D. WITH $6\frac{1}{8}$-IN O.D. INTERNAL FLUSH TOOL JOINTS.

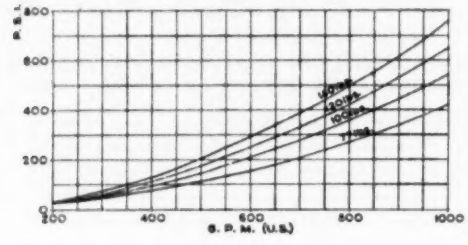

FIG. 5.

DRILL-PIPE PRESSURE LOSSES IN RELATION TO MUD WEIGHT AND FLOW—$4\frac{1}{2}$-IN O.D. WITH $5\frac{3}{4}$-IN O.D. FULL-HOLE TOOL JOINTS.

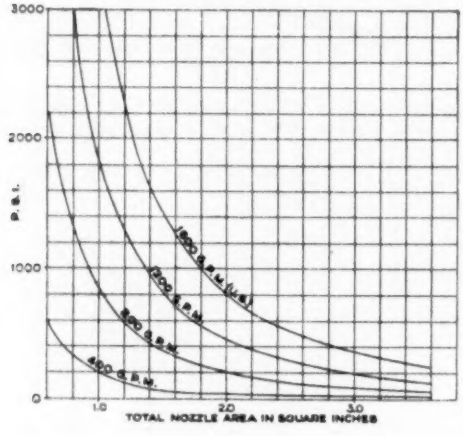

FIG. 6.

BIT-NOZZLE PRESSURE LOSSES IN RELATION TO MUD WEIGHT (77 LB/CU. FT.) AND FLOW.

Should $6\frac{5}{8}$-in drill pipe be available, this would be slightly advantageous to use for the surface hole, but since this pipe is no longer made it is not considered here. Some 6-in outside dia drill pipe has been specially rolled for one of the major oil companies in the U.S.A., but as this is experimental and not yet generally available to the industry, no consideration is given to it here.

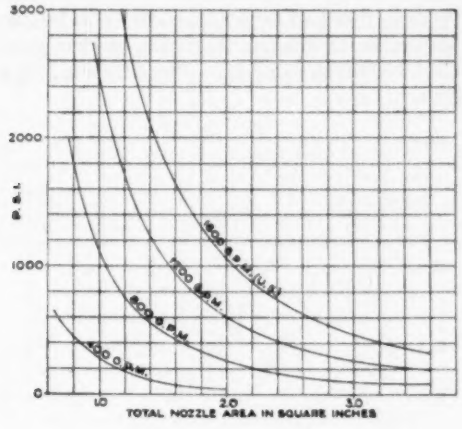

FIG. 7.

BIT-NOZZLE PRESSURE LOSSES IN RELATION TO MUD WEIGHT (100 LB/CU. FT.) AND FLOW.

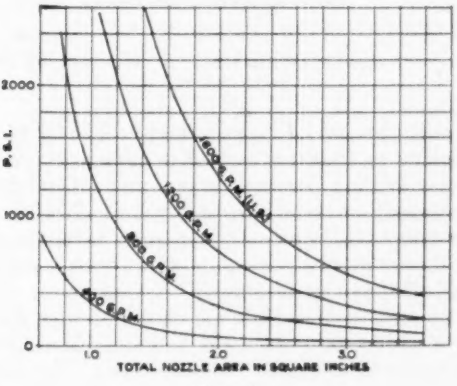

FIG. 8.

BIT-NOZZLE PRESSURE LOSSES IN RELATION TO MUD WEIGHT (120 LB/CU. FT.) AND FLOW.

For drilling between 10,000 and 15,000 ft with the suggested hole size, the only remaining pipe sizes available from the above list are the 5-in outside dia and $4\frac{1}{2}$-in outside dia external upset, both having $6\frac{1}{8}$-in outside dia tool joints, and the $4\frac{1}{2}$-in outside dia internal upset fitted with $5\frac{3}{4}$-in

(6-in optional) outside dia tool joints. It is doubtful whether operators would wish to run $6\frac{1}{8}$-in tool joints in $8\frac{1}{4}$-in hole at depths between 10,000 and 15,000 ft, due to the limited clearance, and therefore only the $4\frac{1}{2}$-in outside dia internal upset pipe with $5\frac{3}{4}$-in outside dia full-hole tool joints remains. This gives a clearance between tool joint and hole of $1\frac{1}{4}$-in all round in $8\frac{1}{4}$-in hole. It should be pointed out here that the drift diameter for the heaviest $9\frac{5}{8}$-in casing available, and which would have to be used in a 10,000 string, is only 0·004 in larger than an $8\frac{3}{8}$-in bit, and for this reason it is considered desirable to cut the diameter of that portion of open hole between 10,000 and 15,000 ft to $8\frac{1}{4}$-in. The following figures are based on $8\frac{1}{4}$-in hole diameter.

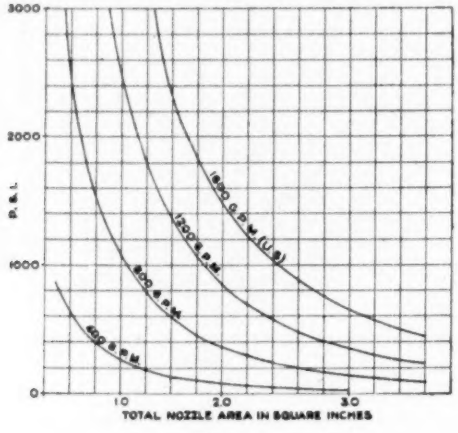

FIG. 9.

BIT-NOZZLE PRESSURE LOSSES IN RELATION TO MUD WEIGHT (140 LB/CU. FT.) AND FLOW.

Having suggested the use of $5\frac{1}{2}$-in outside dia drill pipe with full-hole tool joints for drilling to 10,000 ft and $4\frac{1}{2}$-in outside dia drill pipe with full-hole tool joints for drilling between 10,000 and 15,000 ft, it is necessary to consider the strength of these sizes in tension, allowing some margin for pulling in tight hole. Reference to the pipe tables indicates that the $5\frac{1}{2}$-in outside drill pipe can be run to 10,000 ft with a safety factor of 2·0, but the material will have to be grade " E," having a minimum yield of 75,000 p.s.i. Likewise, $4\frac{1}{2}$-in outside dia drill pipe with internal upsets can be run to 15,000 ft with a safety factor of 1·34 in tension, but again this pipe will have to be made from grade " E " material. As far as the collapse strength is concerned, it is thought so unlikely that the inside of the drill pipe will ever be free of all pressure, that it is not considered necessary to make allowance for this condition. However, if this condition ever should occur, then the available drill pipe, like the current casing, is not strong enough to withstand the high static pressures due to the heavy local muds. Again this condition can be improved only by the introduction of better grades of steel, and for reference the following figures relating to S.A.E. 4340 drill pipe, are given :—

Drill pipe size.	Safety factors.		Mud weight. lb.
	Collapse.	Tension.	
5½ inch at 10,000 ft.	1·11	2·8	140
4½ inch × 18·10 lb at 15,000 ft. . .	0·96	1·87	140

A further assumption must be made in connexion with the pressure drop through the bit (which is taken to be a regular three- or four-way drag type in each size), and this is the total bit-nozzle area.

TABLE II.

Nozzle Sizes and Areas.

Nozzle diameter, in.	Number.	Total area, sq. in.
⅜	3	0·92
,,	4	1·23
,,	6	1·84
,,	8	2·46
⅜	3	1·32
,,	4	1·77
,,	6	2·64
,,	8	3·54
,,	3	1·80
,,	4	2·40
,,	6	3·60
,,	8	4·80

Table II indicates the various total areas due to different numbers of different size nozzles, and the following nozzle combinations are considered for the three-way bits assumed for discussion :—

Bit size in.	Number and size of nozzles.	Total area, sq. in.
8¼	3 × ⅜ in.	0·92
12¼	3 × ⅝ ,,	1·80
17½	6 × ⅝ ,,	3·60
24	6 × ⅝ ,,	3·60

Finally, some basis must be assumed for the pressure drop through the surface connexions. This drop (Fig. 10) is based on the curve given by Nolley, Cannon, and Ragland,[1] except that the drop has been increased in direct proportion to the mud weights, as have all drops and accompanying curves considered in this paper. From the limited records available locally, these curves are thought to approximate Trinidad conditions fairly closely.

Horsepower Requirements.

The calculated total pressure drops and hydraulic horsepowers will now be tabulated for the various sizes of drill pipe and bits suggested above, at

maximum depths. The volumes are based on the deliveries of modern large-power pumps, as stated by the makers, where the pump size is the limitation. Otherwise a maximum annular velocity of 3 f.p.s. will be the factor controlling volume (see Table III). Fig. 12 shows input horsepower

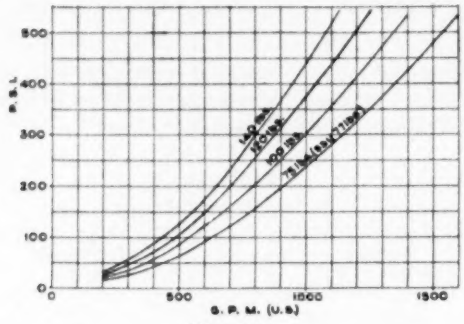

FIG. 10.

SURFACE-CONNEXION PRESSURE LOSS IN RELATION TO MUD WEIGHT AND FLOW.

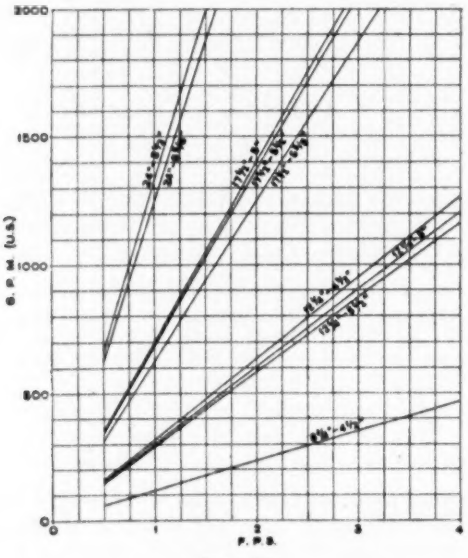

FIG. 11.

CIRCULATION RETURN VELOCITIES IN RELATION TO DRILL PIPE AND HOLE SIZE.

requirements at different depths in each size hole and covers the particular sizes of equipment discussed above; 80 per cent overall efficiency is assumed. If the corresponding curve showing the hoisting horsepower requirements is plotted on the same sheet, an interesting comparison can be made, which indicates clearly, how local deep-well power requirements are governed by hydraulic considerations rather than by the loads to be hoisted. It

TABLE III.

Hole size, in.	Drill pipe size, in.	Depth, ft.	Mud weight, lb/cu. ft.	Mud volume, U.S. g.p.m.	Annular velocity, f.p.s.	Pressure drops in p.s.i.					Hyd. H.P.	Input H.P. (Eff. 80%).	Nozzle area assumed.
						Drill pipe.	Annulus.	Bit.	Surface connexions.	Total.			
24	6⅝	1000	77	1600	1·25	175	Negligible	240	530	945	885	1105	
24	5½	1000	77	1600	1·20	315	,,	240	530	1085	1012	1265	6 × 7/8 in.
17½	6⅝	5000	100	1200	1·95	675	,,	200	420	1295	906	1135	3·6 sq. in.
17½	5½	5000	100	1200	1·75	1200	,,	200	420	1820	1275	1595	
17½	5	5000	100	1200	1·70	2000	,,	200	420	2620	1835	2295	
12¼	5½	10,000	110	800	2·75	1250	75	360	235	1920	895	1120	
12¼	5	10,000	110	800	2·65	2000	75	360	235	2670	1245	1555	3 × 7/8 in.
12¼	5½	10,000	120	700	2·40	1100	80	300	205	1685	690	865	1·80 sq. in.
12¼	5	10,000	120	600	2·00	1250	80	250	150	1730	605	755	
8½	4½ (EU)	15,000	120	350	3·00	1125	225	300	65	1715	350	437	
8½	4½ (IU)	15,000	120	350	3·00	1200	225	300	65	1790	365	456	3 × 5/8 in.
8½	4½ (EU)	15,000	140	350	3·00	1350	300	375	75	2100	430	538	0·92 sq. in.

The annular pressure drops, where shown above, are based on the following formula as given by Stanley C. Moore (see Bibliography) :—

$$P = \frac{0{\cdot}814G^2}{(D_2 - D_1)(D_2^2 - D_1^2)^2}$$

where P = Annular drop per 1000 ft; G = U.S. gal/min.; D_1 = Pipe outside dia in inches; D_2 = Hole size in inches.

should be said here that, whereas the power curve in Fig. 12 shows an initial hydraulic requirement of approximately 800 h.p. when spudding in, and a requirement of about 750 h.p. at 1000 ft when changing to a 17½-in bit, it is fully realized that at these particular points considerably less power would be used in practice, since no operator in Trinidad would use these high pressures and large volumes so near the surface, due to the very commonly occurring crevices in the surface strata, which results in both loss of mud and undermining of the derrick foundations. Nevertheless, it is

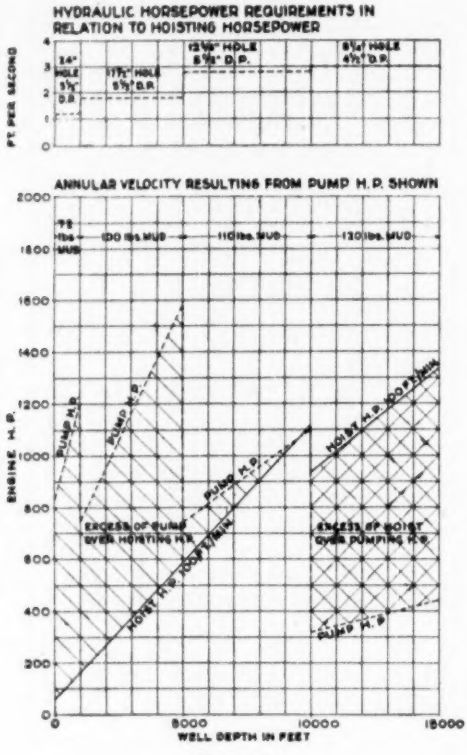

FIG. 12.

felt that the curve, with the above modification, gives a very accurate picture of the power necessary for optimum results.

Before dealing with the other items of major equipment necessary for deep drilling in Trinidad, it should be stated that all the curves and tables presented are based on formulæ put forward by operators and investigators in the U.S.A. These operators, generally, have not had the opportunity to study the behaviour of very heavy muds used locally and, therefore, experimental data covering equipment performance using these muds is sadly lacking. Bearing this in mind, and having regard to the fact that well drilling is no longer a haphazard procedure, it is suggested that every effort

should be made by local operators to carry very full recording instrumentation on their rigs, if economical operations are to be maintained. Recording instruments are no longer a luxury, but a necessity, if correct interpretation and correlation of all the variable factors is desired; it is only by this correlation and the correct interpretation of the results that economic operations to great depths will be possible.

Hoisting Power.

Having estimated the probable pump horsepowers required, it is not proposed to discuss the hoisting-power requirements in detail, since these are practically the same for a given rig, whether steam or internal-combustion power is used.

As pointed out earlier, the necessary rig horsepower is based, primarily, on the hydraulic requirements. If the suggested mud volumes and pressures

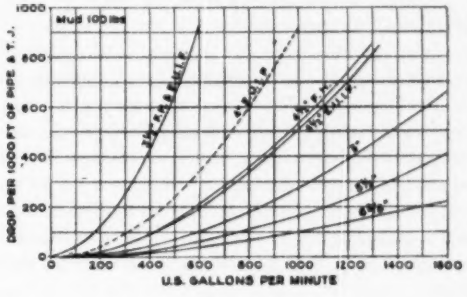

FIG. 13.

COMPARISON OF PRESSURE DROPS IN DIFFERENT SIZE DRILL PIPE PER 1000 FT AND USING A GIVEN MUD WEIGHT.

are analysed, it will be found that until a depth of 10,000 ft is reached, two large pumps must be operated in parallel. Since, on power rigs, the pumps may be driven from the rig engines or independently it becomes necessary to determine which particular arrangement is the most economical, having regard to the hoisting and rotating power required, and to other related factors such as location and accessibility. Reference to Fig. 12 indicates that, with the suggested drill pipe and casing strings, a maximum of some 1300 h.p. will be necessary for hoisting; the power required for the rotary is relatively small. The hoisting horsepower mentioned is conservatively based on an overall drive efficiency of 70 per cent between engines and hook, and allows of pulling pipe at minimum speeds around 100 f.p.m.—this figure generally conforming to standard practice. Bearing the above horsepower figure in mind, it can be readily seen that there are several arrangements possible. Of these, two variations are being considered locally.

One line of thinking indicates that a three-engine drive behind the drawworks, with two large slush pumps driven from this drive, will be sufficient. A smaller slush pump, for mud mixing purposes, is driven independently.

Other indications suggest that a three-engine drive be used, driving one

large slush pump and a smaller slush pump. A three-engine independent-pump-drive unit is used in conjunction with this rig to drive a second large slush pump. The reason for this arrangement is that, after the 12¼-in hole is completed and it is no longer necessary to use two large pumps in parallel, the independent unit may be moved for work elsewhere.

The phrase "large pump" is intended to cover slush pumps in the 600–700 h.p. range, whilst "small pumps" refer to the 200–300 h.p. range.

For purposes of this discussion, a rig unit with three engines driving two large slush pumps, and having an independent small pump drive for mud-mixing purposes, will be considered. Assuming that the required horsepower can be developed by the three engines, this type of arrangement is considered suitable for the following reasons:—

(1) *A combination of individual engine horsepowers will total more than the required* 1600 *h.p. Since modern drilling engines are available in a* 600-*h.p. range when supercharged, a total of* 1800 *b.h.p. would be available for continuous operation.*

(2) *The three engines can be compounded together during drilling operations, thus furnishing adequate input horsepowers for the main pumps, and also leaving sufficient horsepower for the rotary table drive.*

(3) *During the hoisting, cycle standby horsepower is available in case of mechanical failure of an engine; or if necessary, hoisting and pumping can be accomplished simultaneously, so that even under maximum hoisting conditions, one large pump could be almost loaded to capacity.*

(4) *From the standpoint of economics, maintenance will be less with fewer engines operating, and inventory requirements for spare parts will not be as much.*

(5) *As some locations are very limited as to area available for the well site, it is imperative to keep the rig as much one unit as possible, in order to conserve space.*

(6) *Where transportation over poor roads or rough terrain is anticipated, there is a distinct advantage in having fewer loads to haul.*

An alternate arrangement can be made, having a larger number of naturally aspirated low-powered engines, with provision for suitable compounding.

Mention should here be made of the development of a dual-fuel attachment for diesel engines. In view of the comparatively small initial cost this fitting should be beneficial for any diesel engine used for drilling in Trinidad. Natural gas is relatively abundant, and even on exploratory wells where diesel fuel must be used initially, there is every chance that the first well will at least supply gas for further operations. In a proved field natural gas will undoubtedly be available.

In general, there seem to be two prominent engine-drive compounding designs available. One type offers an individual compound unit which is placed upon the three engine frames when in position and direct coupled to the engines. This type of compound may have hydraulic drives incorporated in it, or it may be a straight-mechanical-drive unit.

The other type incorporates a portion of the compound unit in each engine frame. When the engines are placed in position on the drive substructure each frame dowels together, and it is necessary only to connect

the compound chains for operation. As in the first design mentioned above, fluid coupling may be used as a means to clutch the engine, or air clutches may be used for a straight mechanical drive.

Both compound designs are provided with either chain or belt drive to the pumps, but in view of the increasing pump horsepower required in Trinidad, serious consideration must be given to chain drives, since the necessary V-belt sheaves to transmit even 500 h.p., are very cumbersome. In addition, these sheaves apply a very large overhung load to both compound and pump-drive shafts, unless some modification is made to bearing and shaft design. This would probably increase the size and weight of the units still further, and would be an undesirable feature.

Two-speed chain drives for slush-pump operation are now offered. This ensures maximum circulation performance from the pump when the drive is in the high speed, and affords the opportunity while in the low-speed drive, to maintain if necessary, either or both, low volumes and high pressures.

The operator accustomed to the use of steam for drilling purposes is sometimes reluctant to use power-rig equipment, because the positive mechanical power transmitted through the engine compound drive for hoisting and circulation purposes is not sufficiently flexible. To increase power flexibility to the point where it is almost equal to that of steam, both scoop-controlled hydraulic couplings and torque converters have been incorporated in modern rig drives. In addition to the added flexibility, this type of drive is of great benefit in that it absorbs torsional vibrations almost entirely, thus preventing the often very serious damage resulting from these oscillations should they pass from the engine to the drive, or vice versa. It should be mentioned that at the time of writing very large torque converters are not available, but the range of scoop-controlled hydraulic couplings is complete, and includes sizes for almost any drive from that found on the largest drilling rig, to that on the smallest workover rig.

It must also be borne in mind that although pumping operations will require approximately 1600 h.p., the hoisting requirement is only 1300 h.p. Therefore, when the hoisting unit is to be selected, the operator must consider the input horsepower ratings of the various drawworks offered. If he determines that a particular drawworks is adequate for his hoisting and load requirements, but is not rated to accept the combined horsepower of the engines in the engine drive, he must intelligently use the horsepower available for drawworks application.

The majority of the largest hoisting units available on the market to-day should be adequate for the hoisting and casing-load requirements. The average unit incorporates the use of six forward and two reverse speeds to the drum. However, there are units available which offer as many as nine forward and nine reverse speeds. For rotary table operations the speeds offered on the drawworks drive generally have three speeds as a minimum, or nine as a maximum. Some operators prefer to drive the rotary table independently, which eliminates chain wear on the drawworks, and makes available all the drive horsepower for slush-pump operation when the drilling cycle is taking place.

The high and low clutches on modern power drawworks are of the friction

type, and it is noted that both the disc and airflex type are used. In the event of mechnical difficulties or air-supply failures positive-locking drives are available on these clutches.

Due to the heavy loads anticipated, braking capacity is of primary importance. The available range of rim diameters and rim faces for the mechanical brakes on large hoists do not vary very much, but need to be supplemented by an auxiliary dynamic energy dissipator, which may operate on either an electrical or hydraulic principle. Both types of auxiliary brake are designed so that they may be applied to any of the conventional drawworks available to-day.

The controls available on all modern drawworks are air-operated at the driller's position. Engine throttles and clutches, pump clutches, compound clutches, drawworks clutches, and catheads may all be air-controlled.

The crown and travelling blocks should be designed to accommodate, as a minimum, a 300-ton load, and have twelve lines strung when handling the 13⅜-in and 9⅝-in casing loads. Generally speaking, eight to ten lines are strung on deep wells for drilling operation, and ten to twelve lines are used when casing is run. It might be added that this general trend is borne out by an A.P.I. Sub-Committee Report published in April 1948.

In connexion with the size of wire line to be used, it is thought that 1¼-in would be quite satisfactory, since using the minimum accepted safety factor of 3 for a *new* line, and considering an improved plow steel line of 6×19 construction, the safe load that can be carried with twelve lines strung is in the neighbourhood of 260 short tons, which compares with a load of approximately 270 tons when carrying the *dead* weight of 10,000 ft of 53·3-lb, 9⅝-in casing. Nevertheless, a safety factor of 5 should be used as a minimum, for general operations, and it would be desirable to go to 1⅜-in line if longer strings of 9⅝-in casing should be contemplated. This would allow some margin for pulling on tight casing, which is very often kept moving during local cementing operations. It may be said that satisfactory service has been rendered by 1⅜-in lines when used on the drum sizes of current large drawworks.

The swivel should have a minimum capacity of 200 tons. In swivel selection, consideration should be given to design of the wash pipe and its packing, as high standpipe pressures may be expected.

Conventional modern rotary machine design indicates that a standard opening between 20 in and 28 in can be used for deep drilling and, therefore, no undue difficulty should be encountered in selecting a suitable table for the large casing sizes and rotating loads.

Derricks.

A large item of equipment is the derrick and its substructure. It is not proposed to suggest any given sizes or heights, since these are governed by operating conditions, of which the companies themselves are the best judges. However, a few of the factors to be considered will be noted.

Dealing first with the substructure, Trinidad conditions demand one that is higher than usual, due to the need for blow-out prevention equipment. In addition, the performance of any power pump is vastly improved by having a flooded suction, and with the particular mud conditions prevalent in Trinidad, a flooded suction may be said to be essential. To

provide this the well fluid must leave the well at a considerable height in order to be able to flow into the pump suction tanks, and also to allow a drop of about two feet when going through the shale shaker on its way to the tanks. No doubt arrangements could be made to get around these requirements, but in order to conform to a standard set-up, a high substructure is necessary.

Derricks are made in two large conventional sizes—the larger not having been confirmed yet by the A.P.I. These sizes are :—

(*a*) 136 ft high with a 30 ft square floor (A.P.I.)

(*b*) Approximately 180 ft high with a 36 ft square floor. (non A.P.I.)

In the taller derrick the drill pipe can be pulled in fourbles of approximately 122 ft, as opposed to 91 ft stands when operating in a 136 ft derrick. Round trip time would thus be reduced, which is of particular importance when a well is giving trouble due to caving or gas. However, the stands are a little heavier to handle, and this results in a greater load per unit area on the pipe set-back. The actual area required for setting back either 10,000 ft of 5½-in drill pipe, or 15,000 ft of 4½-in drill pipe, when pulled in fourbles, is about 30 sq. ft., whereas if this same pipe is set back in thribles, it will occupy about 38 sq. ft. Since the local practice is to rack pipe in front of the drum, serious consideration will have to be given to the available space on the smaller derrick if this practice is to be continued, whilst still retaining adequate visibility for safe and speedy operation during a round trip. Operators elsewhere are more and more tending to rack to the right of the driller, irrespective of the amount of pipe to be handled. If this practice were applied in Trinidad, it is likely that some local standard layouts would have to be modified. Nevertheless, for deep drilling, it is suggested that the better set-back is to the right of the driller. The choice of derrick and substructure, however, lies entirely with the operator, since both sizes can be built to the necessary strength.

It is not considered necessary to make reference to the other small items of drilling equipment such as the shale shaker, rotary hose and kelly, etc., except to emphasize the very real necessity when designing a rig lay-out, to eliminate as far as possible all restrictions in the mud circuit. Surface connexions should be run with large-bore pipe, and bends should be used wherever possible in place of ells and tees; the largest bore kellys and drill collars should be used wherever practicable and, finally, a large bore hose used if it can be arranged. Whilst these alterations would probably not effect the items of major equipment needed, at least their operation and maintenance costs would be cheaper, and rates of penetration improved, with the resultant overall economies. Only by very careful consideration of these, and all the other factors involved, will really deep drilling become an economic proposition in Trinidad, unless some radical changes in the necessary mud conditions or operating technique come about.

The writers have primarily based their opinions upon information that has been given to them by individual operators in Trinidad. Due to the difficulties experienced, and anticipated, in drilling operations in Trinidad, it is suggested that a closer liaison be established among the operators to openly and officially discuss problems encountered. This will not eliminate

the hazards met in deep drilling, but it will better prepare each operator for a similar situation when it arises.

Until very recently there has been little information recorded by the companies pertaining to slush-pump performance and circulation requirements. As this information is of major importance for deep drilling in Trinidad, steps should be taken to analyse current and future circulation performances and correlate them with anticipated requirements.

Acknowledgments.

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Bibliography.

[1] Nolley, J. P., Cannon, G. E., and Ragland, D., "The relation of nozzle fluid velocity to rate of penetration with drag type rotary bits," *Petrol. Engr*, June 1948, **19** (9), 86; *Oil Gas J.*, 6.6.48, **47** (1), 87.

[2] "Drill Pipe and Tool Joint Design," by Stanley C. Moore. Paper read before American Society of Mechanical Engineers in October 1948.

[3] "Modern Rotary Drilling Machinery and Practices," by W. S. Crake.

[4] "A.P.I. Sub-Committee Report," by O. W. Chanette. A.P.I. Circular S-823, April 1948.

[5] "Drilling Rigs for Deep Wells" by J. R. Mahan. Paper read before American Society of Mechanical Engineers in October 1948.

[6] "To-day's Drilling Rigs." *Oil Gas J.*, 7.10.48, **47** (23), 149.

[7] "Hydraulic Torque Converters & Fluid Couplings for Oilfield Machinery," by H. A. Davis. Paper read before American Society of Mechanical Engineers in October 1948.

[8] "The Operating Characteristics & Requirements of Drawworks Brake Equipment," by R. Griffin De La Mater. Paper read before American Society of Mechanical Engineers in October 1948.

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Oilfield Exploration and Exploitation.

Geology.

160. Characteristics and geologic distribution of coral and other organic reefs. W. H. Twenhofel. *World Oil*, July 1949, **129** (3), 61.—Reefs are mounds of ridges built on the sea floor by corals, algæ, sponges, and a few other organisms. Each of these requires given environmental conditions for reef formation. In general, the reef consists of a complex of various organic materials forming the core, and flanking strata inclined away from it at angles up to 65°. On the seaward side of the core is a subaqueous talus of eroded core material of sand size or larger. This thickens irregularly and passes outwards into lime muds. On the landward side, calcareous muds and lagoonal sediments interfinger with the structureless core material.

The growing reef, on reaching surface, may extend laterally over the marginal sediments with greater extension on the seaward side, where the food content of the water is greater. Sediments deposited over a reef are usually coarser over the core than on the flanks, due to greater agitation of the shallower water, and resulting compaction causes greater thickness reduction on the flanks.

The initial porosity of the core may be high, but the permeability low. Recrystallization, dolomitization, and chertification of the original material may take place as the result of diagenesis, with corresponding changes in porosity and permeability.

Reef building has occurred in every geological period since the Huronian, with much activity in the Permian. C. A. F.

161. The geological interpretation of exploratory wells. P. Weaver. *Oil Gas J.*, 17.3.49, **47** (46), 102.—Nowadays an exploratory well is considered from several points of view. If oil and gas showings are noted, the well is in a region where oil and gas were formed. Are there any reservoir rocks? Logging devices and cores afford evidence on this point. Many so-called sandy shales are actually silt and thin sand beds, and some of the latter may be coarse, indicating proximity to the source where sands might be thicker. Marly shales have over 50% of calcium carbonate, and therefore suggest abundant lime deposition at these horizons, and so elsewhere more calcareous rocks may be found. Fracture zones probably associated with folding may constitute important reservoirs.

The well may also provide structural evidence. Thinning of section may suggest uplift. Caliper logs may indicate the position of faults, because of enlargement at points of shattering. Dip-meter surveys also have pointed to faults. The question should be asked as to what extent the well is a true test of the structure.

G. D. H.

162. Interpretative petrology of sedimentary rocks. G. Rittenhouse. *World Oil*, Oct. 1949, **129** (7), 61.—The philosophy behind interpretative petrology is outlined. Deduc-

tions from composition, texture, and structure can provide information of value to the oil geologist. Of sedimentary properties, composition is inherited from the source rock, shape and roundness are acquired during transport, and orientation and bedding reflect the environment of deposition. Porosity and permeability partly reflect post-depositional changes.

The use of thin-sections in petrogenesis is emphasized, and examples are given.

C. A. F.

163. Sedimentary tectonics and sedimentary environments. W. C. Krumbein, L. L. Sloss, and E. C. Dapples. *Bull. Amer. Ass. Petrol. Geol.*, 1949, **33**, 1859–91.—The purpose of this paper is to examine the problems of tectonism and environment in the light of recent advances in this subject. It is pointed out that the tectonic frame-work of sedimentation largely controls the distribution of sedimentary environments. The major problem in distinguishing tectonic elements and tectonic intensity arises from the interplay between contemporaneous depositional subsidence, and intermittent uplift and erosion. These and other problems and possible solutions are discussed in terms of a hypothetical cycle of deposition. E. N. T.

164. Shoreline processes of the continental shelf. O. F. Evans. *World Oil*, June 1949, **129** (2), 80.—Conditions of transport and deposition of sediments on the continental shelf, which has an area of approx 10 million sq. miles, are similar to those obtaining in past epeiric seas, when oil-bearing sediments were deposited. The shelf may be a " cut and fill " terrace formed by marine erosion and deposition, with the sediments thickening and becoming finer away from the shoreline, or it may represent the flooded margin of the continents. The submarine geology will then be similar to that of the adjacent lands, and superficial sediments will vary irregularly in thickness and coarseness.

Sedimentation conditions on the shelf are complicated by sinking and rising shorelines, and by river-mouth deposition, but the resultant movement of material is offshore, through the agencies of tidal currents, rip currents, and undertow. Locally, movement may be onshore, as exemplified by subaqueous dunes, formed in storm periods parallel to the shoreline, which move shoreward as sediment is deposited on their onshore sides. Multiple ridges and troughs, parallel to the shoreline, known as " low and ball," are fixed at breaker lines during storm periods, and are preserved by transgressing seas. C. A. F.

165. International developments. Anon. *Oil Gas J.*, 28.4.49, **47** (51), 123.—Sylvester 2 in the State of Barinas is reported to have flowed 800 b.d. of 26° oil from the Eocene at 8600–9400 ft. Another successful well has been drilled, and two others are under way.

Casing has been set at 6400 ft in the Puerto Armuelles well in Panama.

The Nar Umar wildcat in southern Iraq has tested 2500 b.d. from a 30-ft interval at about 8360 ft. The Zubair well, 25 miles to the south, is testing intervals below 10,000 ft. An output of 3500 b.d. was obtained at about 7775 ft.

At Redwater, Canada, per well output is being limited to 300 b.d.

One mile south of Burgo de Osma, Soria province, Spain, a wildcat is 800 ft deep, and may go to 5000–6000 ft. A test on the Oliana structure in Lerida province was abandoned at 7622 ft. G. D. H.

166. Record 6827 wells finaled in exploratory drilling. C. Smith. *World Oil*, 15.2.49, **128** (11), 77.—In 1948 U.S.A. had 6827 exploratory wells, compared with 5874 in 1947. 601 new oilfields and 283 new pay horizons in established pools were opened in 1948. 3000 million brl of oil was credited to the discoveries. There were 115 distillate discoveries (seventy new distillate fields) and 140 gas discoveries (103 new gas-fields). 208 field extensions were made.

Tables give yearly from 1937 the numbers of U.S. discoveries of oil, gas, and distillate fields and pays, and by states and districts the footage and average depth of new discoveries in the various categories, together with the dry holes. G. H. D.

167. Exploratory drilling in 1948. Anon. *World Petrol.*, Apr. 1949, **20** (4), 47.—According to F. H. Lahee 8013 exploratory wells were drilled in the U.S.A. in 1948. Their footage was 32,741,097 ft. 1463 were producers. 13% of those located on technical advice were successful; only 3·1% were successful in the absence of such advice. 4296 were new field tests, 1766 outposts, and 1951 new pool tests. New pool discoveries included 379 oil wells, eighty-seven gas wells, and forty-one condensate wells.

172 exploratory wells were completed in Alberta and Saskatchewan (twenty-six oil, eleven gas, one condensate), and twenty-nine in Mexico (six oil, two condensate). G. D. H.

168. Field developments. Anon. *World Oil*, 15.2.49, **128** (11), 82.—The high-lights of 1948 in the principal producing areas are briefly described. Ellenburger production continued to be the prime prospecting objective in West Texas. Numerous Pennsylvanian fields were opened on the eastern rim of the Midland basin. A Strawn field was developed at 3200 ft at Burn-Jones in North Texas. In the Texas Panhandle distillate production has been obtained in the Pennsylvanian in Roberts County. Deep strikes have been registered in North Central Texas in the Bend, Marble Falls, Mississippian, and Ellenburger. Deep exploration was disappointing in East Texas. Oil and gas discoveries were made on the flanks of the South Liberty Batson, Blue Ridge, Pierce Junction, Humble, and Orange salt domes. An important gas and distillate discovery was made in the Peach Point area of the Texas Gulf Coast. South Texas had a number of major strikes, the most important probably being in the Wilcox of the Weesatche area. There were several strikes in the tidelands area of Louisiana. The shoreline play flanking the Pauls Valley uplift continued to provide Oklahoma's most important developments. G. D. H.

169. Wildcatting success shows gain for 1948. Anon. *World Oil*, 15.2.49, **128** (11), 80.—The U.S. had 6182 strict wildcats out of 38,803 completions in 1948. 12·5% of the wildcats were productive. The wildcat results are summarized by states and districts for 1948 and for the period 1937–47. G. D. H.

170. New Cuyama discovery is significant addition to California reserves. G. M. Wilson. *World Oil*, June 1949, **129** (2), 69.—The Richfield Oil Corporation wildcat in the Cuyama valley, 5½ miles southeast of the prolific Russell Ranch field, had an estimated initial production of 5088 b.d. of 34° oil from the Vaqueros. Well-saturated oil sand was drilled from 4095 ft to the completion depth of 4392 ft.

The well was sited on a structural high determined by surface mapping and geophysical work.

Additional structures mapped show similar characteristics to the discovered fields in this area, and plans are being made to test these. C. A. F.

171. Kansans watching Forest City basin strike. Anon. *Oil Gas J.*, 5.5.49, **47** (53), 119.—A well in Wabaunsee County, Kansas (Carter Oil Company 1 Davis) has tested oil in the lower part of the Lansing–Kansas City at 1843–1859 ft, and also in the Viola lime at 3201–3206 ft. The Mississippian was topped at −1064 ft, Hunton at −1563 ft, Viola at −1789 ft. The test is in the southwest corner of the Forest City Basin. G. D. H.

172. The California Company's Bay Marchand field. J. E. Kastrop. *World Oil*, Aug. 1949, **129** (4), 76.—In the Bay Marchand Field, 4 miles offshore from LaFourche, Louisiana, four producing formations have been found between 2873 and 5100 ft. Oil gravity ranges from 20·1° to 40·9°, and no water is produced. Seven productive wells have been drilled, but the limits of the field are not yet defined. C. A. F.

173. New Mexico portion of Permian basin is also hot. Anon. *Oil Gas J.*, 17.3.49, **47** (46), 207.—Northwest of Benedum in the northern Upton–southern Midland county area Magnolia 1-A TXL has the deepest Ellenburger production and a very thick pay section, with indications that production can also be obtained in several shallow pre-Permian pays. In southern New Mexico Amerada Petroleum Corp. 1 BTA State had

good results in a Pennsylvanian lime drillstem test. This well will be carried down to the Ellenburger. It is 7 miles north of the Caprock pool. G. D. H.

174. New Ellenberger strike for New Mexico. Anon. *Oil Gas J.*, 28.4.49, **47** (52), 163.—A well, 1 BTA State in northwestern Lea County, New Mexico, has flowed 46·2° oil at 70 brl/hr in a drillstem test of the Ellenberger at 10,819–10,839 ft. A test at 10,794–11,819 ft gave 294 brl in 4 hr. Some maintain that this pay is Devonian, not Ellenberger. The gas/oil ratio is 25 cu.ft/brl. A Pennsylvanian pay in the same well had a gas/oil ratio of under 2000 cu.ft/brl. The Pennsylvanian was topped at −4400 ft, Mississippian at −6075 ft, and Ellenberger at −6534 ft. G. D. H.

175. Rocky Mountain type structure at Velma Pool, Stephens County, Oklahoma. W. W. Mallory. *World Oil*, July 1949, **129** (3), 68.—Velma Pool is on the axis of the Anadarko–Ardmore geosyncline, a deep Pennsylvanian depositional basin trending northwest–southeast in southern Oklahoma. Pre-Mississippian sediments of the area are nearly 11,000 ft thick, consisting of Cambro–Ordovician limestones, 9000 ft thick, and Siluro–Devonian Hunton limestone and early Mississippian Woodfort chert and Sycamore limestone. Chesterian and Lower Morrow are represented by 2500–3500 ft of a lower shale and an upper sand series. Incipient structures were developed during the Wichita orogeny at the end of the Morrow, and local removal of the upper sand formed sand wedges, now oil bearing. Clastics of mixed type were deposited during the Upper Morrow, totalling 15,000 ft at Ardmore. During the subsequent Arbuckle orogeny, the Anadarko geosyncline was destroyed as a marine basin, and folding and thrusting occurred, with deposition of Cisco conglomerates. Resulting complex structures were base-levelled and buried beneath the basal Permian Pontotoc blanket.

The author describes in detail the stratigraphy and structure of the Velma Pool, which produces from the Pennsylvanian and older rocks. A complex structural pattern is presented beneath the Pontotoc unconformity, and the anticlinal structure is divided by a northwest–southeast thrust, which affects the pre-Permian rocks. The inclination of the fault is steep at the unconformity, but decreases with depth. Five tear faults, transverse to the main thrust, have relatively small displacements.

Ten figures show the location, stratigraphy, and structure of the Velma Pool.

C. A. F.

176. Heavy activity in store for Powder River basin. B. Funk. *World Oil*, May 1949, **129** (1), 61.—Salt Creek is on the southwest side of the Powder River basin and Lance Creek on the southeast side. Salt Creek's peak output was 30 million brl in 1924; it gave 4 million brl in 1948. Lance Creek produced 9 million brl in 1940. The Billy Creek gas-field is on the west edge of the basin, and the Osage oilfield on the east side. The Mush Creek area first produced in the latter part of World War II. There was then great wildcat activity, and in 1948 the output was over 1 million brl.

In 1947 oil was discovered at Adon in the north central part of the basin, in the Minnelusa, topped at 8997 ft. Two dry holes followed. Twenty miles north of Salt Creek Alice Coles No. 1 flowed 241 b.d. from the Lakota at 7710 ft. West of Mush Creek further drilling revealed oil in the Dakota at 6720 ft. Subsequently oil was found between 3500 and 6000 ft, some forty-nine dry holes and ninety producers being completed in 1948. A Newcastle sand producer was completed at Fiddler Creek, midway between the Mush Creek and Fiddler Creek field. At Skull Creek to the east some producers and dry holes were completed. East of Lance the Little Buck Creek discovery was made. G. D. H.

177. Structures of the San Juan basin. F. C. Barnes. *Oil Gas J.*, 31.3.49, **47** (48), 97.—Oil and gas have been found in the Pennsylvanian on the Dore Creek anticline, near Cortez, Colorado, in the San Juan basin. The original oil and discoveries in the San Juan basin were in the Upper Cretaceous in 1911. The Rattlesnake field gave Pennsylvanian oil in 1929. Barker Creek gave Pennsylvanian gas. These two fields are in New Mexico.

In 1948 fifteen geophysical crews and twenty geological parties were active in the San Juan Basin. Forty-one wells were drilled, and six of the twenty-one wildcats were successful. At Boundary Butte oil was found in the Coconino sandstone (Permian) and gas in the Pennsylvanian.

In 1948 the San Juan basin gave 620,000 brl of high-gravity oil and 7,276 million cu. ft. of dry gas. The cumulative oil production at the beginning of 1949 was 13,912,000 brl.

The San Juan basin is bounded by the San Juan mountains on the north and northeast, the La Plata mountains on the southwest, the Nacimiento mountains on the east, and the Mount Taylor volcanic field on the southeast. Some eighty-seven structures are known. Oil or gas has been found in six stratigraphic traps and in one fault trap.

Tables give the structures, with an indication of the surface geology and whether or not they have been tested, the general stratigraphy of the basin, and a list of the oil- and gas-fields with the producing formation. G. D. H.

178. The Greater San Juan basin. J. L. Kerr. *World Oil*, Aug. 1949, **129** (4), 66.—The San Juan basin strictly refers to the structural basin encircled by the outcropping Mesa Verde, but the region contiguous to the Four Corners (New Mexico, Colorado, Utah, and Arizona) is considered as the Greater San Juan basin. The early development of the area is reviewed, and recent discoveries and extensions to existing fields are discussed.

In the major structural unit of the area, the San Juan basin, a sequence of pre-Cambrian to Tertiary beds is exposed, with a total estimated thickness of 12,000–15,000 ft in the central part, where the beds are flat. On the east and west sides, there are one, two, or three lines of gentle folds. Production is from the Pennsylvanian and Upper Cretaceous, with shows in the Devonian and Mississippian. Structures are chiefly domes or anticlines, with occasional stratigraphical traps. Of many prominent structures untested, those in southeastern Utah promise future development of important production and reserves. Recent discoveries include the Boundary Buttes, Upper Valley, and Dove Creek fields.

A table gives geological data for individual fields, and a location map is provided. C. A. F.

179. What became of Benedum field? C. J. Deegan. *Oil Gas J.*, 21.4.49, **47** (51), 184.—The Benedum field has ten Ellenberger, two Silurian (Fusselman), and two Pennsylvanian producers. The Ellenberger producing area is estimated to cover 3500–4000 acres. The water level may be at −8831 ft in the Ellenberger. The seismic maps indicated a big structure with good relief. An oil column of 480 ft is now suggested. The Fusselman productive area may be 5000 acres.

A fault with a throw of about 1000 ft is present, and there may also be minor faulting. Both the Ellenberger and Fusselman pays show high gas/oil ratios, the gas being wet. Gasoline plants are planned.

Drilling time is 100–110 days per well, and the average well may use 125 rock bits. The early wells used about $25,000 worth of special muds; new wells may take $5000 worth. In future 7-in pipe may be set at the top of the Pennsylvanian (about 9000 ft). G. D. H.

180. Geology of the Strake and Squire field area, Duval County, Texas. G. G. Huffman and A. E. Giles. *World Oil*, Oct. 1949, **129** (7), 68.—New producing horizons have recently been discovered in the Strake and Squire fields. Tertiary shales, sandy shales, and complex sand lenses are gently dipping, and are interrupted by a series of normal faults whose displacements increase with depth. Structural nosing against these faults and their change in strike provide traps for oil accumulation. Production is from marginal sands which include the Eocene Strake, Squire, Pettus, and Yegua sands. Source beds are probably dark Jackson and Yegua shales.

By the end of 1948, nineteen producing wells and three dry wells had been completed in the Squire field. Strake field had five pumping and one flowing well. Cumulative production for both fields to Dec. 1948 was 731,469 brl.

Further subsurface work, based on shoreline studies, is justified to locate additional marginal sands.

A contour map on the top of the Squire and Strake sands, and a representative electric log of the section, are given. C. A. F.

181. Origin of shallow structures in West Central Texas. G. H. Brodie. *World Oil*, Sept. 1949, **129** (6), 61.—Most of the shallow oil-bearing structures in West Central

Texas are the result of draping of sediments over incompactible reefs, and, more rarely, over sand buttresses. Tectonic deformation is negligible. Reefs up to 1200 ft thick have been found, which began to grow during the Lower Pennsylvanian or later. Shallow structures in the Cisco and Basal Permian disappear at depth, and are absent in the Cambro–Ordovician below the reef-building limestones.

Cross-sections of three fields are given, which illustrate this type of structure.

C. A. F.

182. Stratigraphy of Frio formation, Orange and Jefferson Counties, Texas. F. Reedy, Jr. *Bull. Amer. Ass. Petrol. Geol.*, 1949, **33**, 1830–58.—This paper describes in great detail the stratigraphy of the Frio formation in the southeastern part of the Texas Coastal Plain. The Frio formation normally consists of more than 2500 ft of marine sands and shales, which have so far produced more than 30 million brl of oil. It is suggested that the Frio formation is divisible into three lithologic units, of which the uppermost consists primarily of sands, the middle unit of marine shales, and the lower unit of sands and shale.

Detailed cross-sections and isopach maps of the area are given. E. N. T.

183. Structure of Grand Saline salt dome, Van Zandt County, Texas. R. Balk. *Bull. Amer. Ass. Petrol. Geol.*, 1949, **33**, 1791–1829.—In certain parts of the Gulf Coast of North America the interior of salt domes is accessible. This paper presents the result of a detailed examination of part of the core of a salt dome which is exposed at Grand Saline, Texas. This salt dome is situated about 60 miles east of Dallas. The structural features of the salt have been mapped on all available surfaces, and a number of specimens have been examined microscopically. In the southeastern portion of the dome, the salt layers dip steeply southeast and south, but in other parts of the dome the layers form an intricate system of folds.

The microscopic features of the salt are described, and it is shown that the anhydrite and halite display a linear alignment.

It is suggested that the absence of fractures and folds, as well as the lack of foreign inclusions, indicates an undisturbed evolution of deformation structure in a nearly homogeneous layered salt mass. In the author's opinion the deformation phenomena in the exposed part of the salt dome are satisfactorily explained by the motion of a layered salt and anhydrite mass upward through the dome. E. N. T.

184. Texas Panhandle strike arouses great interest. Anon. *Oil Gas J.*, 21.4.49, **47** (50), 261.—1 Charles Lips in Roberts County, Texas Panhandle, has flowed 35° oil from the Mississippi lime at 8900–8970 ft. The well is believed to be on a high trend parallel to and northeast of the Amarillo uplift. A fair gas and distillate show is said to have been obtained from the Pennsylvanian at about 5500 ft. G. D. H.

185. Another important reef strike for west Texas. Anon. *Oil Gas J.*, 7.4.49, **47** (49), 123.—A well in southwest Borden County has given 22 brl/hour in a drillstem test from a reef phase thought to be the Canyon limestone. This well is 6½ miles north of the Vealmoor field of northern Howard County.

The pay is at 7910–7940 ft. G. D. H.

186. Canada's problems : transportation and refining. C. O. Nickle. *World Oil*, May 1949, **129** (1), 213.—When Leduc was opened in 1947 Alberta was producing about 19,000 b.d. By the end of 1947 the output was 25,000 b.d., and it reached 40,000 b.d. at the end of 1948. In mid-March 1949 the production was 58,000 b.d.

Leduc–Woodbend has reserves of 250 million brl, mainly in a Devonian coral reef at 5200–5400 ft. Some oil and gas occur in Lower Cretaceous sands at 4100 ft, and in a Devonian dolomite at 5000 ft. The productive area is now 15,000 acres, with 215 wells giving 30,000 b.d. Redwater has reserves estimated at over 300 million brl in Devonian reef limestone at 3150–3500 ft. There is a 35–40-ft oil column with an effective water drive at Leduc. The Golden Spike discovery, 5 miles west of the north end of Leduc–Woodbend, found 544 ft of oil pay.

At Joseph Lake a well has flowed 528 b.d. on a ½-in choke, from the Viking sand. 50 miles northwest of Leduc, the Madison at Barrhead has given 24-gravity oil at

4900 ft. Between Leduc and Redwater at Bon Accord the D2 Devonian has given light oil at 3300 ft.

Early in April some 50 million acres in Alberta were leased for exploration, and sixty-five geophysical parties were at work. There is also some exploration in north-east British Columbia, south and central Saskatchewan, and southwest Manitoba.

Markets must now be found outside the Prairie provinces, where the 1949 demand may be 65,000 b.d. The refining capacity is being raised to 54,000 b.d. A pipeline is to be built from Leduc–Redwater to Regina. G. D. H.

187. Canada's possibilities now look enormous. Anon. *Oil Gas J.*, 14.4.49, **47** (50), 143.—1 Golden Spike, 4 miles west of Woodbend, met the reef at 5363 ft, and after coring and testing oil and gas recovered 60 ft of salt water and 2900 ft of oil at 5861–5881 ft. This water level is below that at Woodbend. 1 Golden Spike and other outsteps are based on seismic work. G. D. H.

188. Development in West obscures eastern Canada activity. Anon. *World Oil*, June 1949, **129** (2), 228.—Exploration and development in Ontario by Imperial during 1948 resulted in an increased production of 33%. Principal objectives are shallow Silurian Salina–Guelph formations, and several new oil- and gas-fields have been discovered. C. A. F.

189. Devonian discovery possible in Canada's Stettler area. Anon. *World Oil*, June 1949, **129** (2), 234.—Ellis 1, 100 miles northeast of Calgary, has penetrated 50 ft of Devonian D-2 pay at 5240 ft. A drill-stem test showed 20 brl per hr on $\frac{1}{2}$-in choke. The entire Devonian section will be drilled. C. A. F.

190. Northeastern Mexico. E. J. Guzman. *Oil Gas J.*, 17.3.49, **47** (46), 165.—The Tertiary basin of northeast Mexico belongs to the Rio Grande embayment. Geological and seismic work began in the Reynosa area before 1938. Fifty-six exploratory and development wells were drilled. The Rancherias, La Prosa, and Chilpitin structures, which produce gas, have been found. In the Reynosa area itself gas and oil shows were found, especially in the Vicksburg–Frio. Starting in 1942 gravity meter and seismic work was done over about 2200 sq. miles. In 1944 1 Mision was spudded, being on the extension of the Penitas structure. This well produced gas and distillate. Pemex has since drilled six wildcats and thirteen field wells and semi-wildcats in the Pemex area. Three gas producers and one oil producer were completed from the wildcats. There were four gas-wells and one oil-well among the field wells. Seismic work has indicated twenty structures in this area. All the six structures tested are anticlines, but production is closely related to stratigraphic changes.

Camargo has closure of about 300 ft, and is roughly 3 miles long, with its axis northwest–southeast. Gas has been found in the Vicksburg–Frio at 2167 ft and 2278 ft.

1 Valadeces was drilled on an indicated local closure on the east flank of the Camargo anticline, about 3 miles east of the Camargo wells. This encountered a gas sand at 5974 ft, but the pressure declined rapidly.

On the Mision structure the closure is largely stratigraphic with pinch-out to the west. The Jabali structure is 17 miles south-southeast of the Camargo wells. It is about 7 miles long. The Rio Bravo wells were on a small closure to the east. These found oil and gas shows in the Vicksburg, and gas shows in the Frio. On the crest of the Jabali structure 1 Norias also had oil and gas shows in the Frio and Vicksburg.

The Reynosa anticline is elongated north-northwest–south-southeast. A well found two oil and three gas sands. There is stratigraphic closure in the producing sand. Wells on the Trevino structure found no commercial production. The Brasil structure lies south-southeast of the Trevino structure. Two commercially productive gas and distillate sands have been tested in the Frio at 6890 ft and 7220 ft. The 18 de Margo structure is 10 miles long. A well was drilled to 10,175 ft. Several promising gas sands and a possible oil sand were tested, but all appeared to have low permeabilities.

A number of maps and cross-sections are included, and a table lists the salient data for a number of wells at Mision, Camargo, Valadeces, and Reynosa. G. D. H.

191. Cuban activity resumed. S. Scholle. *World Oil*, Oct. 1949, **129** (7), 221.—A number of major oil companies have concessions to exploit Cuba's oil. A deep test,

2 miles offshore in Cardenas Bay, has topped the Eocene at 1636 ft, and traps are anticipated in the Lower Cretaceous Aptichus Limestone below 8000 ft. Three more deep tests are proposed.

Cardenas Bay is floored with asphalt, and along the north coast there is evidence of domes similar to those off the east coast of Mexico. Asphalt and gas seeps are said to be widespread.

Of the three previously discovered fields, Motembo and Bacuranao are shut down. The Jarahueca field is producing 600 b.d., and an extension is planned. C. A. F.

192. Crude moves from Velasquez, Colombia's twelfth oil field. Anon. *Oil Gas J.*, 24.3.49, **47** (47), 139.—There are two producing wells giving 700 b.d. from the Teran–Guaguaqui properties. 1 Velasquez, completed in 1946, stopped in basement at 8455 ft, and gave 311 b.d. of 27·1° A.P.I. oil from 6945–7120 ft. The gas/oil ratio was 663. 2 Velasquez found water, and 3 Velasquez tested 565 b.d. from 7608–7666 ft, on a $\frac{1}{4}$-in choke. Wells 4 and 5 were dry. Trapping is believed to be due to faulting, with oil in the Guadas (Eocene). The discovery was on a seismic prospect.

G. D. H.

193. New exploration scheduled for Eucador. Anon. *World Oil*, Sept. 1949, **129** (6), 222.—A new wildcat is scheduled for drilling in the Ecuadorian "Oriente." Three wildcats were completed in 1948. Cangaime 1 was abandoned at 3450 ft. Oglan 1 was dry after drilling to 9438 ft. Tiputini 1 was abandoned at 5515 ft. Subsurface Tertiary beds are, however, favourable, and there were oil showings.

In southwestern Ecuador, extensions of existing fields continue. New and shallow areas have been developed on the Ancon Peninsula, and in 1948, sixty wells were drilled, of which fifty-three were producers. Deep drilling has so far proved unsuccessful. C. A. F.

194. Venezuelan completion announced by Richmond. Anon. *Oil Gas J.*, 17.3.49, **47** (46), 60.—The Ensenada discovery lies between the Boscan–Albaricos field and the west side of Lake Maracaibo. Boscan–Albaricos has twenty-three wells. The field has a potential of about 12,000 brl of heavy oil. G. D. H.

195. Schoonebeek field drilled up, but Dutch continue exploration. Anon. *Oil Gas J.*, 14.4.49, **47** (50), 63.—Forty-one wells have been drilled at Schoonebeek, and in August 1948 the production was 11,400 b.d. The 1948 output was 495,539 tons. A deep well on the crest found high-pressure gas in fractured Permian limestone in drilling to 9137 ft. $1\frac{1}{2}$ miles from Schoonebeek at Dalen a sand-bearing oil has been found at 2840 ft. G. D. H.

196. Discovery of new oil field in Emsland area is indicated. Anon. *World Oil*, June 1949, **129** (2), 243.—Ruehlertwist 2, northwest of Lingen (western Germany), has found porous saturated sand from 2255–2285 ft in the Bentheimer sandstone, which is found in the neighbouring Georgsdorf and Emlichheim fields. The structure is believed to be a local high on the eastward extension of the Emlichheim–Schoonebeek feature. C. A. F.

197. Exploration in Germany meets with increasing success. Anon. *World Oil*, Oct. 1949, **129** (7), 238.—Ruehlermoor 1, several miles east of the important Ruehlertwist discovery, flowed 150 b.d. from the Bentheim Sandstone, from 2085–2155 ft. Tests of the Dichotomiten sandstones in this well indicated this zone to be also productive.

Suderbruch 1, a wildcat in Lower Saxony near Schwarmstedt, found 46 ft of oil sand at 6757 ft, and produced 240 b.d.

Hohenhorn 12, 3 miles southwest of Schwarzenbek, on a salt-dome, produced 20–45 b.d. of heavy oil with relatively high sulphur content from two zones of the Jurassic Lower Dogger.

Geophysical surveys are being carried out in northwestern Germany, with emphasis on outlining a structure in the tidelands area of the North Sea in the Duhnen–Neuwerk–Schaarhoern area, believed to be a continuation of the Heide–Meldorf fields, which produce from good Tertiary accumulations. C. A. F.

198. Po Valley discovery may lead to significant production. Anon. *World Oil*, July 1949, **129** (3), 229.—On recompletion a test well near Cortemaggiore, southeast of Milan, flowed 175 b.d. of light oil and 70,000 cu. ft. of gas from 5000 ft. It is estimated that reserves can yield 21 million cu.ft/day. There are other indications of oil in the Po Valley. C. A. F.

199. Gas well completed in Upper Po Valley. Anon. *Oil Gas J.*, 31.3.49, **47** (48), 62.—Cortemaggoire 2, about 22 km east of Piacenza, has been completed at 1535–1540 m. The gas flow was not measured, but the closed-in pressure was 2206 p.s.i. There was some condensate. Cortemaggoire 1 had gas shows in the Quaternary at 560 m and 970 m. In a side-track hole at 1585–1610 m a drillstem test gave 70 m of oil and salt water. This well is still drilling. The structure was outlined by seismic work.

7 km northeast of Lodi gas was discovered at Ripalta. 13 km from Ferrare gas is reported to have been found at Montalbano (880,000 cu.ft/day). G. D. H.

200. Russians said to have found oil in Austria. Anon. *Oil Gas J.*, 14.4.49, **47** (50), 63.—At Matzen, 20 miles northeast of Vienna, a 1400-brl well has been completed by the Russians. The first well drilled by the Russians in 1947 had oil shows before running into difficulties; the second blew out with high-pressure gas. The Matzen structure was defined by geophysics and core drilling in 1937–38. G. D. H.

201. Ethiopian operations begin with spudding of Gumburo 1. Anon. *World Oil*, June 1949, **129** (2), 237.—Gumburo 1, 475 road miles southeast of Dire Dawa, has been spudded after extensive geological surveys of the Ogaden area. It is planned to drill to 15,000 ft. C. A. F.

202. Three Sinai peninsula fields promise greater Egyptian output. Anon. *World Petrol.*, Mar. 1949, **20** (3), 54.—A well at Wadi el Feiran, 92 miles south of Suez, has produced 9 brl/hr on a $\frac{1}{4}$-in choke from 6505–6570 ft in the Miocene Globigerina marls. Basement was at 6627 ft.

Sudr has fourteen wells with production at an average depth of 2750 ft, in basal Miocene sands and conglomerates and Eocene limestone. Daily production is about 14,000 brl. Sudr is 25 miles south of Suez.

Asl, 10 miles south of Sudr, has five wells, some of which have given large outputs on test. The structure is apparently complex, with buried faults.

Last year Egypt produced about 35,000 b.d., and consumed 45,000 b.d.

The new oil law encourages rapid exploration of licensed areas, because the charges rise yearly. Exploitation leases are half the exploration areas, and have a 15% royalty. Additional leases carry 25% royalty. Royalty may be credited against lease rental. Lessees must sell up to 20% of the oil or products to the Egyptian government at 10% below world market prices. Other conditions relate to staff and to drilling. G. D. H.

203. Successful Arabian wildcats may open two new producing fields. D. M. Duff. *Oil Gas J.*, 10.3.49, **47** (45), 48.—The Haradh wildcat, 120 miles south of Ain Dar, gave good results in a test believed to be in the Arab D zone. Ain Dar has three shut-in wells capable of producing 32° oil from about 6900 ft.

The Fathili well, 70 miles northwest of Dammam, has given oil at 1000 b.d. on test, and is drilling below 9980 ft. Abu Hadriya, 15 miles to the northeast, has a pay at about 10,000 ft. Fathili and Haradh are on seismic features.

Aramco has carried out air and ground reconnaissance over its 440,000-sq. mile concession. Seismic, gravity, and structure drilling parties also have operated.

In 1948 Saudi Arabia produced 142,852,989 brl. (Abqaiq 105,902,423 brl, Dammam 33,426,992 brl, and Qatif 3,523,574 brl). At the end of 1948 ninety-nine wells had been drilled, eighty-eight being capable of production. G. D. H.

204. Afghanistan to invite aid of U.S. oil companies. Anon. *World Oil*, Aug. 1949, **129** (4), 244.—American aid is sought to develop Afghan petroleum resources. The area believed to be the most promising lies north of the Hindu Kush mountains. A foothills belt merges with a plains basin, containing up to 15,000 ft of Cretaceous and Tertiary sediments. On the south side of the Orus, *en echelon* anticlines parallel the

mountain trend. Active oil and gas seeps dot the region, and the presumed reservoir rocks show residual oil at the mountain outcrops. The larger anticlines, which are not strongly faulted or folded, may be expected to hold commercial pools in Lower Cretaceous and Eocene sands. C. A. F.

205. New producers encourage Iraq exploration programme. Anon. *World Oil*, June 1949, **129** (2), 236.—Several structures have been located by extensive geophysical work in the area west of Basrah, and three wells have been drilled. The Nar Umar well produced 2500 b.d. on test, at a total depth of 8360 ft. The Zubair well, completed for 3500 b.d. initial production, found oil at 7775 ft. The Ratawi well, 30 miles west of Zubair, is drilling below 7140 ft.

Exploration also continues in northern and central Iraq, and several wells are being drilled. C. A. F.

206. Syria becomes hot spot of Middle East oil. Anon. *World Oil*, May 1949, **129** (1), 232.—After unsuccessful wildcats at Baflioum (8666 ft) and Dola (6163 ft) the Iraq Petroleum Co. abandoned about one-third of its Syrian concessions, and this area has been taken up by another party. Wells have been spudded to the east at Abba and Gouna.

West of Basra a wildcat is being drilled at Al-Zudair, and northwest of Basra oil has been found at Mar Umr, where a test gave 2500 b.d. from 8317 ft. A third test is being drilled at Ratawi.

In Qatar four shut-in producers are estimated to be capable of 6000 b.d. A pipeline is being built.

A number of important pipelines are under construction or planned, and in some cases awaiting on political developments. G. D. H.

207. Horizontal drilling increases yield of Australian oil field. L. Ranney. *Oil Gas J.*, 7.4.49, **47** (49), 48.—Up to 1941 forty-four wells had been drilled in the Lakes Entrance field in an area of 15 sq. miles. Thirty-six had shows of oil. Production ranged 4·9–110 I.G/day. The structure is a monocline with production from 35 ft of glauconitic sand at 1200 ft. Beneath is freshwater sand, and the basement occurs at 1300 ft. The glauconitic sand contains many thin bitumen lenses. It is fine-grained. There is no gas. The sand contains 12,000–20,000 brl of oil per acre. A 10-ft dia shaft has now been sunk, and test holes, 1½ inches in dia, have been drilled from the bottom of the shaft to penetrate the sand horizontally. The longest at present is 200 ft. A flow of 25–30 b.d. has been obtained. G. D. H.

208. Philippines to invite new operators. D. Andres. *World Oil*, Sept. 1949, **129** (6), 231.—A test drilled in the northern part of Cebu in 1947 reached basement at 9950 ft, but was abandoned in spite of oil indications. In 1948 a well drilled on Bondoc Peninsula was abandoned at 1372 ft. A second well, 1000 ft to the west, was tested from 1750 to 2250 ft, and flowed 250 b.d. for a short time.

Detailed surveys have been made in Luzon, Leyte, Cebu, and Panay, with extensive reconnaissance of other islands.

Four sedimentary basins, the Cagayan Valley, the Central Plain of Luzon, the Iloilo Basin of Panay, and the Cotobato Valley in Mindanao, are believed to be the best prospects for oil development. Oil seeps are found in the Bondoc Peninsula, southern Mindanao, northwest Leyte, and Cebu Island. Tertiary beds, which are present in all the areas, are partly equivalent to the oil-bearing horizons of the East Indies. C. A. F.

Geophysics and Geochemical Prospecting.

209. Geophysics, geology and oil finding. L. L. Nettleton. *Oil Gas J.*, 17.3.49, **47** (46), 103. In favourable areas the maps obtained in reflection-seismograph work may be turned over to the geologist as accurate representations of one or more subsurface horizons. In less favourable areas the geophysicist must use more geological knowledge before the geophysical map becomes usable for subsurface work.

In gravity and magnetic surveys there is no unique solution, and so a greater knowledge of the geological possibilities is needed in interpretation. Density data are vital,

and a vertical density distribution would be most helpful. Not all strong gravity features have a counterpart in the known geology, even when they are regional.
G. D. H.

210. Salt mine test proves earth penetration by radio waves. Anon. *World Petrol.*, Mar. 1949, **20** (3), 62.—Radio waves have been transmitted from a surface transmitter to a receiver in a salt mine, involving passage through 700 ft of sediments, some fresh-water, 25 ft of cap-rock with brine, and 400 ft of salt and 100 ft of air. The transmitter is designed to minimize reflection at the earth's surface. The frequency was 1602 kilocycles. G. D. H.

211. 1948 brought increase in geophysical activity. Anon. *World Oil*, 15.2.49, **128** (11), 81.—At the end of 1948, 559 geophysical and core-drilling crews were active in the U.S.A. There were 427 seismic crews, eighty-four gravity crews, eight magnetometer crews, and forty core-drilling crews. 188 geophysical crews and five core-drilling crews were operating in Texas. Louisiana had 103 prospecting parties.

A table gives by states and districts the numbers of geophysical crews of various types and of core-drilling crews operating at the end of 1947 and 1948. G. D. H.

212. Prospecting in Northwest Arkansas. K. R. Burns. *World Oil*, June 1949, **129** (2), 74.—Several wells drilled near Fayetteville, Madison county, in the Palæozoic Ozark Highlands area, have yielded evidence of oil and gas in the Mississippian, but no commercial production has been obtained. Potential oil-bearing horizons are shallow, and include the Fayetteville, Boone, St Peter, and Arbuckle. Preliminary reconnaissance using radarology has indicated a basin, but further drilling is needed to confirm this. Closer investigation of local areas in northwestern Arkansas is necessary to evaluate oil possibilities. C. A. F.

213. A method of prospecting for Kansas Shoestrings. O. E. Campbell. *World Oil*, Aug. 1949, **129** (4), 62.—Studies of fluorologs from wells drilled in Shoestring sands indicate that there is excess mineralization above the oil accumulation, and that the path of hydrocarbons escaping from the reservoir is outwards and upwards. Fluorologs of wells drilled over an accumulation show a section barren of oil traces, whereas dry stepout wells show oil traces throughout the section.

Fluorographic methods of exploration, using surface and subsurface techniques, can be effective in locating other types of accumulation. C. A. F.

214. Exploration in the Philippines. Anon. *World Petrol.*, Mar. 1949, **20** (3), 64.—The Philippines have several sedimentary basins which are considered favourable for oil occurrence. A deep well on Cebu had showings.

Concessions to foreign companies are limited to 2,471,000 acres; after exploration half must be returned to the government. Leases are for terms up to twenty-five years, with possible renewal for a like period.

A well is being drilled on the Bondoc peninsula of Luzon. Tertiary deposits on Panay may be 9000 m thick. The Dingle limestone varies from 0–2000 ft, and its surface is very irregular. There is a good velocity contrast, but difficulties arise in seismic work because of the lenticularity of the formation. It is uncertain whether an indicated geophysical high is a structure or a reef.

A stratigraphical column is included, and there is a description of the seismic equipment used in the exploration. G. D. H.

Drilling.

215. Statistical study of accuracy of some connate-water resistivity determinations made from self-potential log data. M. R. J. Wyllie. *Bull. Amer. Ass. Petrol. Geol.*, 1949, **33**, 1892–1900.—A statistical analysis is presented of the comparison between thirty-nine connate-water salinities computed from electrical logs and the comparable measured resistivities. The practical usefulness and the limitations of the method of calculation are reviewed. It is shown that there is a significant correlation between the magnitude of the errors of interpretation and the resistivities of the muds used in the logging process. E. N. T.

216. The core recorder. C. Millinson. *Petrol. Tech.*, Feb. 1949, **1** (2), *A.I.M.M.E. Tech. Pub. No.* 2542, 33–5.—The core recorder is placed inside the core barrel. It contains a clock which turns a drum carrying a chart. An external serrated wheel presses on the inside of the barrel and rotates when the entry of core causes the recorder to be moved. The rotation of this wheel is transmitted to a style which draws a record on the chart.

The recorder clock marks the time of the events, and shows when coring began and ended, whether core entered the barrel continuously, or whether and when any was lost. G. D. H.

217. Rotary rig with hydraulic drive. H. Krekler. *Erdöl u. Kohle*, 1949, **2** (10), 442–5.—The Haniel and Lueg I.C. or electrically driven rig with the Ljungstrom hydraulic torque converter is described and its advantages enumerated. S. E. C.

218. Slight decline shown in report on rotary rigs running abroad. Anon. *Oil Gas J.*, 7.4.49, **47** (49), 47.—In Mar. 457 rigs were believed to be running outside the U.S.A. and the Russian-controlled areas; 279 were in South America. The Middle East and Egypt had forty-nine, while Europe had thirty-nine.

A table gives the rigs operating by countries in Dec. 1948 and Mar. 1949. G. D. H.

219. Semi-automatic power-operated drilling machinery. M. E. True and B. L. Stone. *Petrol. Tech.*, Feb. 1949, **1** (2), *A.I.M.M.E. Tech. Pub. No.* 2543, 27–32.—In order to deal with drilling to greater depths and to reduce the crews' physical efforts in making round trips under such conditions semi-automatic, power-operated drilling equipment has been developed which enables round trips to be made without the drillpipe being touched by hand. The equipment is experimental and comprises hydraulically operated tongs which perform the stabbing, spinning, and tonging operations, and two power-operated racking units, to carry the pipe to and from the centre of the hole and to place it on the mat and in the rack. The equipment is remotely controlled by the derrick-man and tong operator by means of hydraulic valve-levers and electric switches. The rate of handling is approx the same as with conventional equipment, but there is absence of the fatigue which slows crews, and no interference due to bad weather. The equipment has been used on two 10,000-ft wells.

In addition to a description of the equipment, a series of pictures illustrates the operation of the equipment. G. D. H.

220. Gulf of Mexico floating drilling tender. C. P. Besse and G. W. Osborne. *Petrol. Tech.*, Apr. 1949, **1** (4), *A.I.M.M.E. Tech. Pub. No.* 2590, 87–91.—In offshore drilling there are advantages in placing a minimum of equipment on the platform and using a floating drilling tender or drill barge anchored nearby. In the Gulf of Mexico a boat less than 250 ft in length may have difficulty in keeping anchorage in the heavier northwesters and southeast gales. Two types of war-surplus barges of 2000–2500 tons meet the general requirements for drilling tenders. For continuous operation under all but hurricane weather, the mooring must permit the boat to rise and fall with the waves, and prevent impact loading of the moorings as a result of surging of the ship. To achieve this, use must be made of constant-tension mooring winches or heavy anchor chains. $2\frac{1}{16}$-in stud-link anchor chain was adopted. These had an ultimate strength of 341,000 lb, and were handled by windlasses capable of a pull of 120,000 lb. The three bow chains were 900 ft long, and the three stern chains 1080 ft. A seventh chain of $1\frac{1}{4}$ in and 1080 ft long was used at the bow to facilitate directing the bow towards the drilling platform. The boat is manœuvred to take heavy seas on bow or stern. For a wind of 50 m.p.h. it was estimated that the load on one broadside anchor would be 47,500 lb. 10,000-lb patented anchors were employed, backed up by pile anchors in the three stern positions. The latter were 60-ft 14-in H-beams driven 10 ft into the ocean bed, and attached to the patented anchors by chain with about 90 ft of slack. Tests have not been carried out, but in one case a holding capacity of over 120,000 lb was indicated.

A bridge free to move horizontally and vertically provides one connexion between barge and platform, and there are flexible lines for mud, water, oil, and cement, as well as power and communications.

Diagrams show the moorings and the lay-out of the decks and holds, while the materials loaded for drilling the first well are listed. G. D. H.

221. Evolution of drilling mud technology by the Régie Autonome des Pétroles from 1944 to 1949. A. Thomas and J. Furnal. *Bull. Ass. franç. Tech. Pétrole*, Aug., 1949, No. 76, 45–104.—The first section of this paper discusses the functions of a drilling mud, and refers to viscosity, gel strength, measurement of pH, the detection of electrolytes. The succeeding section deals with mineral colloids—kaolinites and montmorillonites—and presents data on the viscosity, free water, and filter-cake for a number of samples, together with some dehydration curves and curves showing the relationship between free water and temp. In the third chapter there is a discussion of organic colloids, including sodium alginate and carboxymethylcellulose, with tabulations of the properties of muds treated with these substances. Particular reference is made to the resistance to contamination. The fourth chapter is concerned with the effects of additives such as phosphates, tannins, humic acids, and carbonates. Again the discussion is supplemented by tables showing the principal properties of treated muds. Reference is also made to weighting agents and to fillers. The last chapter deals with the evolution of muds in the French fields, and describes some of the results obtained with these and other muds. G. D. H.

222. Outline of weather and wave forecasting techniques. A. H. Glen and J. E. Graham. *Petrol. Tech.*, Feb. 1949, **1** (2), *A.I.M.M.E. Tech. Pub. No.* 2546, 49–54.—In offshore drilling adverse weather and wave action are the greatest hazards to safety and efficiency. Because direct action against these is at present impracticable, forecasting of their incidence is the best solution to this problem. Wave height, and wind speed and direction are of great importance in offshore drilling. The forecasts for the Grande Isle district have been prepared twice daily for 24- and 48-hr periods. Observations reported by the U.S. Weather Bureau permit the construction of a three-dimensional picture of the atmosphere in the area of interest, and a forecast is based on the past sequence of weather conditions. Local observations are needed to show how large-scale influences are modified, and to evaluate the accuracy of the forecasts. Good communications are necessary.

The height of ocean wind waves is a function of wind speed, fetch, and duration. Wind waves and swell are changed on entering shallow water. In the Gulf Coast area a rapid change of wind direction from south to north may cause trouble. Line squalls are recognizable, on standard meteorological charts, and so an initial warning may be given 6–8 hr in advance. Squalls can give 5–6 ft waves and high gusty winds which are dangerous.

There is no technique for predicting hurricane movements far in advance, but 6–12-hr predictions are usually reliable. Hurricanes can cause high waves, even in shallow water, and hence before they arise equipment must be secured and personnel evacuated.

The ultimate goal is to anticipate working conditions, not weather conditions, and to arrange operations accordingly. Transportation and the running of long strings of casing require careful consideration in this connexion. G. D. H.

Production.

223. A study of oil and gas conservation in the Pickton field. J. R. Welsh, R. E. Simpson, J. W. Smith, and C. S. Yust. *Petrol. Tech.*, Mar. 1949, **1** (3), *A.I.M.M.E. Tech. Pub. No.* 2564, 55–65.—The Pickton field of Hopkins County, Texas, was discovered in 1944, and produces from the Bacon limestone of the Lower Glen Rose at depths of 7888–7896 ft. The stock-tank oil in place is estimated at 19,577,000 brl, and a recovery of 16·7% by primary methods is predicted. The dissolved gas/oil ratio is 2220 cu.ft/brl, and the reservoir volume factor 2·42.

Detailed data are presented on the reservoir liquids and on volumetric balance calculations, while curves show past and future performance with and without pressure maintenance. Six plans for returning gas to the reservoir are discussed, and the recoveries and economics are considered for returning gas at a constant rate with extraneous gas in the early stages, or without extraneous gas, for various plant sizes. A gasoline plant would be needed, and the pool would have to be worked as a unit.
G. D. H.

224. Methane hydrate at high pressure. R. Kobayashi and D. L. Katz. *Petrol. Tech.*, Mar. 1949, **1** (3), *A.I.M.M.E. Tech. Pub. No.* 2579, 66–70.—Experimental data have been obtained for the three-phase hydrate–water-rich liquid–vapour methane–water system over the range from 72·5° F and 4900 p.s.i. to 83·9° F and 11,200 p.s.i. The pressure cell had glass windows through which the formation and decomposition of the hydrate could be observed. It was necessary to super-cool the liquid–vapour system by as much as 12° F to cause hydrate formation at the higher pressures. When formation occurred the temp was raised slowly until three phases appeared. Extrapolation of the curves suggests that a solid hydrate should form at 100° F at about 40,000 p.s.i.

The methane–water system shows two distinct critical loci between the so-called liquid and vapour phases.

The data are presented in tabular and graphic form, and are discussed with the aid of diagrams. G. D. H.

225. Method of establishing a stabilized back-pressure curve for gas wells producing from reservoirs of extremely low permeability. E. R. Haymaker, C. W. Binckley, and F. R. Burgess. *Petrol. Tech.*, Mar. 1949, **1** (3), *A.I.M.M.E. Tech. Pub. No.* 2545, 71–82.—A method is described whereby it is possible to determine reliable back-pressure potential curves and stabilized back-pressure curves for wells in the Hugoton gas-field. The stabilized back-pressure curve thus obtained can be used to find actual rates of gas production into a pipeline for pre-determined well-head working pressures. It is also satisfactory for the design of gas-gathering systems and for the sizing of orifice meter settings. The technique described saves about 88% of the gas normally vented by long-duration back-pressure tests where pipeline pressure is such that it is necessary to use a critical flow prover or choke nipple to measure rates of flow during testing.

The productivity indices for gas wells producing from low-permeability reservoirs when plotted against time on logarithmic paper show a declining straight line or slightly curved trend similar to the oil-well declining-productivity indices which have been described.

The method is believed to be applicable to many fields besides Hugoton.

G. D. H.

226. Theoretical generalizations leading to the evaluation of relative permeability. W. Rose. *Petrol. Tech.*, May 1949, **1** (5), *A.I.M.M.E. Tech. Pub. No.* 2563, 111–26.—An expression for wetting-phase relative permeability is derived from fundamental considerations based on the Kozeny equation for flow and Leverett's expression for capillary retention. Predicted results agree with existing experimental data. Similarly an expression for the relative permeability of the non-wetting phase has been supported by experimental data.

General consideration has been given to the problem of three-phase permeability phenomena and gas/oil ratios.

Capillary pressure data essentially identify the distribution of pore widths with a range of fluid-phase saturation configurations under static conditions, and this fact can be used to derive an expression for relative permeability relationships.

G. D. H.

227. Evaluation of capillary character in petroleum reservoir rock. W. Rose and W. A. Bruce. *Petrol. Tech.*, May 1949, **1** (5), *A.I.M.M.E. Tech. Pub. No.* 2594, 127–42.—Improved apparatus and techniques for determining the capillary pressure–saturation relationship are described. A multi-core apparatus simplifies experimental work in relatively homogeneous reservoirs.

The capillary pressure–saturation relationship and the capillary retention relationship are discussed. In the former case curves have been calc to show the effects of varying interfacial tension, contact angle, permeability, and porosity. A nomogram is given for relating the capillary pressure and capillary retention curves.

The data from capillary pressure tests can be interpreted to reflect the distribution, orientation, shape, and tortuosity of the pores; the interfacial and interstitial surface area; and the relative permeability to the wetting phase. G. D. H.

228. Construction of apparatus for the study of porosity. A. Houpert. *Rev. Inst. franç Pétrole*, 1949, **4** (3), 95–102.—When a porous solid is placed in a vessel of known vol, it is possible to infer the vol of the solid matter from the behaviour of the air contained in and surrounding the specimen when it is subjected to changes of pressure. This volume, together with the bulk of vol of the specimen, permits the calc of the porosity of the specimen. This principle has been applied in the designing of several pieces of apparatus for the determination of porosity or of the solid vol only. Field and laboratory equipment is described, and the essentials of the design and the accuracy are discussed in detail. G. D. H.

229. Action of surface forces on the equilibrium and movement of hydrocarbons in reservoir rocks. A. Houpert. *Rev. Inst. franç. Pétrole*, Apr. 1949, **4** (4), 107–18.—The following points are discussed in some detail : surface and interfacial tension and the angle of contact, together with some of the effects of dissolved gas ; capillary pressure and displacement pressure ; the relationship between capillary pressure and saturation ; relative permeability ; distribution of fluids in a virgin reservoir, the amount of interstitial water, and the transition zones ; the action of surface forces in the drainage of reservoirs : (*a*) when there is an expanding gas cap, (*b*) advancing edgewater, (*c*) neither gas cap nor mobile edgewater, (*d*) invasion by drilling-mud filtrate. G. D. H.

230. Permeability determination. W. Correns and H. Schumann. *Erdöl u. Kohle*, 1949, **2** (10), 439–42.—Simple apparatus for the determination of the permeability of both cemented and unconsolidated rocks is described, and the method of calculation outlined. S. E. C.

231. Capillary pressures—their measurement using mercury and the calculation of permeability therefrom. W. R. Purcell. *Petrol. Tech.*, Feb. 1949, **1** (2), 39–48.—The determination of capillary pressures by forcing mercury into the evacuated porous solid has been found to give results which are reasonably similar to those obtained by the porous-diaphragm technique. Using mercury, an entire capillary pressure curve of 20 to 30 points can be determined in a few hours instead of weeks as required for establishing equilibrium with porous diaphragms. Small, irregular fragments can be used as well as shaped samples, and the range of pressures investigated can be five to ten times that of conventional methods.

An equation has been derived which relates the permeability of a porous medium with its capillary pressure curve. This relationship includes a lithology factor. Experimental data are given to show that the relationship provides a fairly reliable means of calculating permeability from capillary pressure data. By combining the measurements of the capillary pressures of drill cuttings with the permeability equation it is possible to estimate the permeability of cuttings. G. D. H.

232. Formation testing. J. Nougaro and J. Boitte. *Rev. Inst. franç. Pétrole*, 1949, **4** (6), 240–50.—Pressures recorded while running the formation tester and before setting the packer may throw light on the state of the mud and reveal the presence of unsuspected oil or gas horizons. Pressures recorded during the test serve as a guide to events during this period. They also indicate whether or not the equipment is functioning properly when a test is being made.

10–15 min seems sufficient to give a stable value for the initial formation pressure. When flow takes place at the surface the static and flowing bottom-hole pressures, together with the rate of production, permit the calc of the productivity index. An approx value for the productivity index may be obtained when there is no flow at the surface.

The string of pipe used in drillstem testing differs from the ideal production string. Comparison of the productivity index obtained in drillstem tests with that on completion is useful. If there is a difference between the data for the open and cased hole this may be due to imperfect perforation, to mud invasion, etc. When there are several productive horizons it is useful to know their pressures, and the inter-relations of productivity index and static pressures may be important in explaining some types of well behaviour.

Frequent pressure surveys may provide data on the efficiency of production tech-

nique. New wells may show whether the drainage area of old wells has reached them. Pressures observed in drilling indicate the pressures needed for gas injection. The pressures may also show whether there are breaks in the continuity of the producing horizon.

Pressure recorders associated with formation testers are subject to rough usage. A description of the Johnson type E recorder is given, together with an account of its use. G. D. H.

233. Gas hydrates of carbon dioxide–methane mixtures. C. H. Unruh and D. L. Katz. *Petrol. Tech.*, Apr. 1949, **1** (4), *A.I.M.M.E. Tech. Pub. No.* 2578, 83–6.—Experimental data are presented on the conditions of hydrate formation for mixtures of carbon dioxide and methane. In addition, there are data on conditions of hydrate formation for carbon dioxide–water mixtures.

Equilibrium constants for carbon dioxide (the mol fraction in the gas phase divided by the mol fraction of carbon dioxide in the hydrate) were calculated using equilibrium constants for methane obtained previously. The quadruple point was found to be 49·8° F and 653 p.s.i.a. The hydrate of carbon dioxide appears to be less dense than water. G. D. H.

234. Relation between pressure and recovery in long core water floods. J. N. Bretson and R. V. Hughes. *Petrol. Tech.*, Apr. 1949, *A.I.M.M.E. Tech. Pub. No.* 2591, 100–10.—Differing conclusions have been reached in laboratory water-flood studies on the relationship between pressure gradients and oil recovery, probably because of variable procedures and unnatural conditions and materials. Nineteen water floods have been made on two long sandstone cores, each 4¼ in in diameter, the First Venango core being 51 in long and the Third Bradford core being 12 in long. The former had a brine permeability of 49 mD and 18% porosity, and the latter a brine permeability of 15·3 mD and 16·9% porosity. The Venango core had flooding pressure gradients of 0·1–11·15 p.s.i/ft and the other core 1·02–49·5 p.s.i/ft. These gradients embraced the rates of water advance for comparable rocks in the Bradford field. The cores were not extracted, but were flushed with crude before use. A live crude and natural brine were used in the experiments.

The experiments showed increased recoveries and lower residual-oil saturations with increased flood-pressure gradients and flood velocities. There was a marked fall in recovery for both cores at very low flood velocities. The pressure versus recovery relationship held up to the point of water break-through and up to the 100 to 1 produced water-to-oil ratio point. G. D. H.

235. Estimation of reserves and water drive from pressure and production history. E. R. Brownscombe and F. Collins. *Petrol. Tech.*, Apr. 1949, *A.I.M.M.E. Tech. Pub. No.* 2589, 92–9.—A study has been made of the material balance–fluid-flow method of estimating reserves and degree of water drive from pressure and production history data for a gas-distillate field known to be surrounded by a water zone of wide extent. A consideration of the effect of random pressure errors shows that in the case examined a standard deviation of 3½ p.s.i. in each of ten pressure surveys permits the estimation of the reserves with a standard deviation of 8% and the water drive with a standard deviation of 15%. The technique is believed to be particularly valuable when reservoir pressures are accurate within a few pounds, and it may also be employed with less accurate pressure data if a relatively large reservoir pressure decline occurs early in the life of the field, as in an undersaturated oilfield.

Discussion of the paper is appended. G. D. H.

236. Effects of transient conditions in gas reservoirs. D. T. MacRoberts. *Petrol. Tech.*, Feb. 1949, **1** (2), *A.I.M.M.E. Tech. Pub. No.* 2547, 36–9.—Assuming that a well is initially closed in and that pressure throughout the reservoir is uniform, a disturbance will pass out from the well on opening the latter. If a logarithmic pressure distribution is established it is shown that the pressure change is propagated with a definite velocity, and that the time to reach a certain point varies inversely as the permeability and directly as the porosity; it is practically independent of the rate of production.

The Monroe gas-field is calculated to have a transient time of the order of years.

Thus part of the field can be effectively depleted, but a connected part may have virgin pressure. The transients complicate tests intended to test continuity by interference. G. D. H.

237. Drillstem testing. J. Nougaro and J. Boitte. *Rev. Inst. franç. Pétrole*, Apr. 1949, **4** (4), 119–29.—Before the advent of drillstem testing, the testing of any horizon was a slow and costly business, and might involve the setting of several sets of casing. All drillstem-testing equipment has a packer to isolate the formation from the mud pressure. Valves are opened, and the fluid which enters the drillstem is eventually recovered after closing the appropriate valves and releasing the packer. The tester can be used in open hole, or when a rat-hole has been drilled, or between two packers. It can also be used with casing perforations, and to test cement jobs as well as to find the producing gas/oil ratio at various levels in a perforated section.

A number of different testers are available. All have packers, circulating and equalizing valves, a choke, temp and pressure recorders. They differ in the methods of opening and closing the valves, whether by rotation or translation, or both. The Halliburton, Owens, Eastman, Shaffer, Hayward, MacReady, and Security testers are described. The principle of the packer is described in detail, and there are brief notes on the circulating valves and the anchor pipe. The main features of the pressure record are described.

A too heavy mud at the bottom of the hole may hinder the operation of the tester. Pieces of mud, metal, or rubber may act similarly. In using a rat-hole it must be central so that the shoulders are symmetrical. The rock must be suitable for the packer seat. No attempt should be made to test a long section of the hole, because this involves a very long column of mud entering the drill-pipe. This exerts a big back pressure. Care must be taken to observe the level of the mud in the hole during a test. A fall in level shows the packer is not functioning properly. G. D. H.

Oilfield Development.

238. International developments. Anon. *Oil Gas J.*, 28.4.49, **47** (52), 68.—In Feb. oil production outside the U.S.A., Russia, and eastern Europe, was about 3,338,500 b.d., 1,400,200 b.d. coming from the Middle East. Russia and eastern Europe are believed to have given 728,000 b.d.

A table gives the Jan. and Feb. 1949, production by countries.

Oil concessions covering about 9 million acres are reported to have been granted to Shell and the Gulf Oil Corporation in Tunis.

The Abba test in Syria has reached 6200 ft, and the Gouna test 2800 ft.

A drillstem test at about 4600 ft, in a well 14 km from Beziers, France, is reported to have shown a small amount of oil. G. D. H.

239. Foreign crude output dropped 65,000 brl daily in January. Anon. *Oil Gas J.*, 31.3.49, **47** (48), 61.—In January oil production outside the U.S.A. and Russian-dominated areas is estimated to have averaged 3,306,300 b.d. Venezuela gave 1,246,000 b.d., Canada 44,000 b.d., the Middle East 1,352,500 b.d. Russian output is estimated to have been 612,000 b.d., and the Roumanian output 80,000 b.d.

Tables give the January output by countries, and the Venezuelan output by companies and fields. G. D. H.

240. A.P.I. and A.G.A. committees report gain in oil and gas proven reserves. C. J. Deegan. *Oil Gas J.*, 10.3.49, **47** (45), 44.—U.S. crude oil reserves were estimated to be 23,280, 444,000 brl at January 1, 1949; natural-gas reserves were placed at 173,870,000 million cu. ft. Extensions and revisions added 3,804,600,000 brl of liq. hydrocarbons in 1948, and new discoveries added 461,164,000 brl. Extensions and revisions in 1948 added 9,769,483 million cu. ft. of gas, and new discoveries added 4,129,089 million cu. ft.

Tables give the reserves and production by states, both for gas and oil, together with the changes in 1948. G. D. H.

241. Petroleum reserves enlarged by 1,000,000,000 barrels. Anon. *World Oil*, 15.2.49, **128** (11), 156.—At the beginning of 1948 the U.S. crude reserves were estimated at

21,487,685,000 brl; at the end of the year the figure was about 22,500 million brl. In the eleven-year period 1937–47 25,701,224,000 brl of new crude reserves was proved in completing 181,398 wells (average 141,684 brl for each well). For 1947 17,613 wells proved 2,464,570,000 brl (139,929 brl/well). Hence it is inferred that the 21,761 oil wells completed in 1948 would add about 3000 million brl of reserves.

At the end of 1948 there were about 439,963 active oil wells, an increase of 11,441 during the year.

Natural-gas liquid reserves at the end of 1948 were estimated to be 3,350 million brl, an increase of about 100 million brl during the year.

Tables show the proved reserves by states at the beginning and the end of 1946, the U.S. reserves at the end of each year from 1936, with the nature of the finds, the U.S. reserves, including condensate from 1918 onwards, and the natural-gas liquids reserves by states at the beginning and end of 1946. G. D. H.

242. Reserves : petroleum. W. E. Pratt. *Oil Gas J.*, 17.3.49, **47** (46), 112.—The energy content of the U.S. proved gas reserves exceeds that of the proved liq oil reserves. In 1913 the U.S. consumption of petroleum was 600,000 b.d. To-day it exceeds 6 million b.d. During this period the reserves have risen from 3000 million to 25,000 million brl. The total volume of the earth's petroleum resources is unknown, because they have been little explored. U.S.A. has only about one-sixth of the volume of rocks believed to be favourable for oil. These rocks vary in richness, but they serve as a basis for estimating the reserves in favourable areas still not explored. Studies in the U.S.A. indicate that on the basis of past experience the land area should ultimately give about 100 million brl of oil. Correspondingly, the world should have about 600,000 million brl. 128,000 million brl has been discovered, and 55,000 million had been produced to the end of 1947. These figures do not include the resources of the continental shelf areas. For the shelf areas off Louisiana, Texas, and California the reserves may be 12,000–30,000 million brl.

It appears that in the immediate future available supplies should exceed demands.

The intercontinental depression comprising the low-lying lands of the Persian Gulf, Black, Caspian, and Red Seas and the eastern end of the Mediterranean Sea has immense oil reserves. The area round the Caribbean is second in importance. Oceania is a third important area. The Arctic Sea may be of importance in respect of oil, and there are seepages on the periphery. Other petroleum provinces are in the interior basins of North and South America, European Russia, and Siberia. G. D. H.

243. Known reserves rose to 8·3% in 1948. Anon. *World Petrol.*, Apr. 1949, **20** (4), 47.—The U.S. oil reserves at the end of 1948 were estimated to be 23,280,444,000 brl, 1,792,759,000 brl more than at the end of 1947. 1948 production was 2,002,448,000 brl. The gas reserves at the end of 1948 were 173,869,340 million cu. ft., the natural-gas liquids amounting to 3,540,793,000 brl.

A table summarizes the changes between 1947 and 1948. G. D. H.

244. U.S. crude production faces stricter proration. Anon. *World Oil*, 15.2.49, **128** (11), 140.—There are indications that for 1949 a daily average output of 5,625,000 brl of oil will meet U.S. needs. This is above the 1948 average, but less than the 5,680,000 b.d. in Nov. and Dec. 1948. 2,016,200,000 brl was produced in 1948, 160 million brl more than in 1947. 84% of the oil came from Texas, California, Louisiana, Oklahoma, and Kansas. Texas' contribution was 45% of the total.

Tables give the U.S. yearly totals and daily average oil outputs yearly from 1918; the 1941, 1947, and 1948 outputs by states, and the yearly production of each state from 1859 onwards. G. D. H.

245. Well completions and footage highest in history. Anon. *World Oil*, 15.2.49, **128** (11), 102.—39,319 wells were completed in the U.S.A. in 1948, the footage being 135,040,218 ft (new wells 134,659,093 ft). There were 36,659 wells seeking oil or gas, 1854 water-input wells, and 651 wells deepened. 21,760 wells found oil, 346 distillate, and 3041 gas. Wells were drilled in thirty-one states, but over 75% were in California, Illinois, Kansas, Louisiana, Oklahoma, Pennsylvania, and Texas. Texas had 12,264 wells.

Tables give the U.S. completions and footage yearly from 1925, the types of comple-

tions yearly from 1918, with the total for 1859–1917, and the types of completions and footage by states for 1948. G. D. H.

246. Natural gas production continues spectacular gains. Anon. *World Oil*, 15.2.49, **128** (11), 148.—U.S. marketed natural-gas production in 1948 was estimated to be about 4,900,000 million cu. ft. Nearly 7500 miles of new gas pipelines were put into operation. The proved recoverable natural-gas reserves at the beginning of 1948 amounted to 165,900,000 million cu. ft.; 90,000,000 million cu. ft. was in Texas and 23,500,000 million cu. ft. in Louisiana.

Tables give the number of natural-gas wells, the marketed production, and its value annually from 1918; the reserves at the end of each year; the natural gas marketed yearly in each state from 1906 onwards and its total value; the recoverable reserves of natural gas in each state at the end of 1946, with the changes in 1947 and the types of reserves; and the recoverable natural-gas-liquid reserves by states at the end of 1946, with the changes in 1947 and the nature of the reserves. G. D. H.

247. Natural gasoline output up 9·4% during 1948. Anon. *World Oil*, 15.2.49, **128** (11), 152.—In 1948 the U.S. produced 144,763,000 brl of natural gasoline and allied products. Texas produced an average of 193,000 b.d., and Louisiana 46,000 b.d.

Tables give the annual U.S. output of natural gasoline and allied products from 1918 onwards, and the outputs by states from 1911 to date, with the total value in dollars. G. D. H.

248. Drilling depth records set in seven states. Anon. *World Oil*, 15.2.49, **128** (11), 110.—The record depth of 17,823 ft was attained in 1947 in Oklahoma. In 1948 a well was abandoned at 17,696 ft in California. Texas' deepest well was 16,655 ft reached in 1945. Louisiana has a 16,106-ft well.

A table lists the deepest well in each state or district, while another table gives the successive depth records since 1927. G. D. H.

249. Superior well, holder of world depth record, drilling ahead. Anon. *World Oil*, 10.3.49, **47** (45), 42.—1 Limoneira, 6 miles east of Ventura, California, has been drilled to more than 18,500 ft in six months at a cost of about $500,000. The last core at 18,428–18,438 ft was still in Pliocene. The maximum deviation recorded was 3° at 9087 ft, and at 16,660 ft it was 1·5° off vertical. An electric log was run at 18,111 ft, the bottom-hole temp being about 280° F. 9⅝-in casing was set at 11,209 ft. At present the drill-pipe load is about 320,000 ft. G. D. H.

250. Producing depth record broken once in 1948. Anon. *World Oil*, 15.2.49, **128** (11), 162.—A well in West Poison Spider field, Wyoming, has produced oil from 14,309 ft in the Second Frontier formation. A well was completed at 14,255 ft in the Weeks Island field of Louisiana. Five states now produce below 13,000 ft. California's deepest production is at 13,907 ft, while Oklahoma's deepest production is from the Bromide at 13,250 ft in the Northeast Bradley field.

Tables give the successively deepest producers and the producing well depth records by states and districts. G. D. H.

251. 23,393 wells to require pumping equipment. R. L. Dudley and E. Sterrett. *World Oil*, 15.2.49, **128** (11), 137.—23,393 U.S. oil-wells were expected to be fitted with lifting equipment in 1949. The cost of the installations is likely to be 2¼–3½% above 1948 prices. About $46,151,000 is earmarked for oil-well maintenance in 1949, and $15 million will be expended in Texas.

A table summarizes, by states, the 1949 lifting equipment needs giving the numbers of wells put on lift in 1948 and expected to go on lift in 1949, the 1948 oil-well completions and the numbers of oil-wells flowing at the end of 1948 and abandoned during 1948, together with the number of pumping units to be maintained in 1949, and the expected maintenance costs. G. D. H.

252. Rocky Mountain area shows rapid growth. M. Goodin. *World Petrol.*, May 1949, **20** (5), 44.—The first oil discovery in the Rocky Mountain area was at Florence in 1862. Within the last five years there has been renewed activity over wide areas.

Deep basinal production has been obtained at Worland (oil) and Church Buttes (gas), Wyoming. Previously the discoveries had been on the margins of the basins. Other deep wells have had discoveries. Wyoming now has 163 oilfields, and sixteen were found in 1948, while new deep-pay zones were opened in nineteen fields. At Lost Soldier production has now been found in the Pennsylvanian Amsden, Madison, and Cambrian. Wertz also gives Cambrian production. Oil has been found in the Mesaverde (Upper Cretaceous).

Rocky Mountain oil production has doubled in the past eight years. Rangely with 55,000 b.d. leads. In 1948 Wyoming gave 55,227,357 brl, Colorado 17,792,782 brl, and Montana 9,304,972 brl. Over half Wyoming's production is black oil. Eastern Utah has been the scene of further activity. Shows have been found in wildcats, but no sustained production. Attention has been paid to the Basin and Range area of Utah and Nevada, and work has been done in southwest Montana and north central Idaho.

Three oil discoveries were made last year in the Big Snowy formations of central Montana. Further attention is being given to North and South Dakota. The discovery of gas and distillate at Dove Creek, Montezuma County, Colorado, has directed interest to the San Juan basin. Oil has been discovered at Boric in the Denver basin.

The refinery capacity of the Rocky Mountain area is about 240,000 b.d.; daily throughput is now about 160,000 b.d. The major pipeline outlet is to Kansas City, and its capacity is 25,000 b.d. G. D. H.

253. Canadian production rose 60% during 1948. Anon. *Oil Gas J.*, 10.3.49, **47** (45), 47.—In December 1948 Canada averaged 40,244 b.d. of oil, 37,785 b.d. coming from Alberta. Leduc averaged 21,326 b.d.

A table gives the outputs for the leading fields. G. D. H.

254. Alberta's oil development and problems. T. A. Link. *World Oil*, July 1949, **129** (3), 205–8.—Oil developments since the Leduc discovery in 1947 are summarized, and problems encountered by operators in relation to government regulations, prices, proration, and markets are discussed.

Five figures show the generalized geology of western Canada, and production and refining data. C. A. F.

255. Alberta reaches new production peak. J. L. Irwin. *World Petrol.*, Mar. 1949, **20** (3), 50.—In 1948 Alberta is estimated to have produced 10,973,538 brl of oil. Leduc gave more than 4,500,000 brl. At Turner Valley three lower porous zones have been found. Leduc passed Turner Valley daily output in June 1948. Leduc–Woodbend has 174 producers, and a reserve estimated at over 200 million brl. Oil is obtained from the D2 and D3 horizons under water drive. Redwater also produced from Devonian limestone. Its length may be 10 miles and width 2 miles, with reserves of 80–160 million brl indicated.

Hanna has two oil-wells and a large wet-gas well. Craigmyle 1, 16 miles northwest of Hanna Pete, found oil and gas. Joseph Lake No. 1, 20 miles southeast of the Leduc discovery, flowed 35° oil from the Viking sand. Schoepp No. 1, 4½ miles west of Woodbend, encountered oil and gas.

Tables give the Lloydminster and Leduc production in 1947 and 1948, and Canada's oil and gas production by provinces for the same years. G. D. H.

256. Germany struggles for higher oil output. A. M. Stahmer. *World Petrol.*, June 1949, **20** (6), 42.—A slow recovery of Germany's oil industry began in 1947. In the first half of 1948 178,724 ft was drilled in northwest Germany, and in the second half 340,314 ft. The production was correspondingly 295,910 tons and 339,330 tons.

750 wildcats have been drilled in the past fifteen years. Four pools were producing in 1930; now there are twenty-eight. About 5·3 million tons of crude has been obtained from fields found since 1930, and their remaining reserves are 10–12 million tons. Forty-two wildcats in 1948 yielded a possible new field in Stemmerberg 4, from the Cornbrash at 3945 ft. The Ascheberg wildcat blew gas from fissures in the Upper Cretaceous and Senonian. Oil shows were found at Hohenassel–Osterlinde, Eitzendorf, Hardess, and Duingen. The Georgsdorf field was extended west, the area now totalling 1600 acres. A new block was discovered in the Hademstorf field, while a second

Rhaetic producer was completed at Thoren. The Ruehlertwist wildcat on the prolongation of the Coevoorden structure found oil-impregnated Bentheim sandstone. In the neighbourhood of Celle oil-impregnated Cretaceous sands were found in complicated structures.

A table gives the 1947 and 1948 production by fields and companies, the total for 1948 being 4,446,680 brl. There is a map of the Georgsdorf structure. G. D. H.

257. East Indies production at 80% of prewar volume. Anon. *World Oil*, May 1949, **129** (1), 228.—The Seria field was discovered in 1929, the Miri field having been found in 1911. The latter produced from broken sand lenses. At the beginning of the war Seria covered 3200 acres, including offshore developments. Shallow sands occur at 1600 ft, but better sands are below 6000 ft, and these may have 400 ft of producing section. All the production is Tertiary, the paraffin-base oils being 19–33° A.P.I. Currently Seria produces 63,000 b.d.; at the beginning of the war the output was 16,000 b.d. In spite of destructive action before capture by the Japanese, the latter are believed to have produced 10,799,000 brl from Seria. The field now has fifty-nine flowing wells and eighty-four on gas-lift. Oil from Miri and Seria is refined at Lutong.
G. D. H.

Transport and Storage.

258. Cathodic protection in an oil refinery. D. Holsteyn. *Oil Gas J.*, 10.11.49, **48** (27), 319.—Experience has proved that cathodic protection of pipelines and tank bottoms in contact with soil is practical and economical.

An average reduction in maintenance costs of about 70% has been obtained at a cost of about 35% for cathodic protection based on a maintenance expenditure of 100%.

Installation design was based on curves pertaining to the behaviour of a ground rod and a series of ground rods which discharged current to earth.

Cost per installation varies from $1700 to $2200, capacity from 10 V 50 amp to 15 V 100 amp and theoretical life is fifteen years.

Multiple anodes were used for a desired current distributor.

Causes of failures of pipelines are examined. The equipment must be properly maintained, and personnel should be trained.

Five figures illustrate the article. G. A. C.

259. Use of ammonia in control of vapour-zone corrosion in storage tanks. F. T. Gardner, A. T. Clothier, and F. Coryell. *Oil Gas J.*, 10.11.49, **48** (27), 238.—The mechanism of vapour-zone corrosion due to hydrogen-sulphide-bearing crude oils includes condensation of drops of moisture on surface of tank metal, solution of H_2S and O_2 in condensed moisture, partial oxidation of H_2S and establishment of local corrosion cells over areas in contact with the condensed droplets.

As a result of laboratory and field tests with ammonium carbonate as a source of ammonia, field applications were made with anhydrous ammonia, and three tables show results on sour-crude storage tanks. Cost of ammonia for providing protection against H_2S corrosion is lower than for protective coatings, and if tank is subsequently used for sweet crudes, there would be no need to continue use of ammonia.
G. A. C.

260. A pipe-line flow controller for partial loops. G. P. Jennings. *Oil Gas J.*, 17.11.48, **48** (28), 93.—Controls on a partial loop pipeline system belonging to the Phillips Petroleum Co., situated from Borger, Tex., to East St. Louis, Ill., and consisting of over 350 miles of partial loops divided into twenty-two partial loops are described.

The insert-type flow nozzle with recovery cone was used as the differential producer. The loop controller was placed at the beginning of each partial loop on the discharge side of the station.

The accuracy of the loop controls has been checked by inserting a heavily concentrated dye solution in undyed gasoline at the pump station and noting arrival time of dye in each line at end of loop.

Four figures illustrate the article. G. A. C.

261. New method for internally cleaning and coating pipe lines in place. D. H. Stormont. *Oil Gas J.*, 3.11.49, **48** (26), 66.—Cleaning is accomplished with chemicals, steel lathe cuttings, and other mechanical devices, using compressed air as a means of propulsion.

After application of primer coat, one plastic top-coat is applied; during which the line is flood-coated with a full line of coating between two pressure plugs; then it is reapplied by the pressure and wiping action of the rearmost pressure plug.

The applications can be made in pipeline length up to about 10 miles per treatment.

G. A. C.

262. Launching of sealine 2B. Anon. *Fluid Handling*, 1949, **1**, 9–13.—The method employed in launching a 12-in 16,341-ft offshore pipeline at Lutong, Sarawak, British Borneo, is described. The technique involved the prelaunching of 4620 ft of the line the remainder of the line then being drawn offshore by the tug at an average of 2·4 m.p.h. in one operation.

The line was first welded into lengths of 165 ft, which were primed with red lead and then with bitumen, and then into 2000-ft lengths. Lagging was then applied, and the line welded into one 16,341-ft length. Joints were reinforced by three $\frac{3}{8} \times 3 \times$ 9-in butt straps. Final test pressure was to 700 p.s.i. G. S.

Refinery Operations.

Refineries and Auxiliary Refinery Plant.

263. Bibliography of investment and operating costs for chemical and petroleum plants. W. I. Barnet. *U.S. Bur. Mines, Rep. Invest.* 7516, Oct. 1949, pp. 53.—Prepared in connexion with investigations into the production of fuel from oil shale, this bibliography was designed to enable economic evaluation of estimated investment and operating costs. The 185 references cover: (1) equipment and plant investment costs and (2) equipment and process operating costs, and relate to matter published in the period 1930 to Sept. 1948. Each reference has a short abstract, and adequate indexes are given. G. S.

264. Continental expands Ponca City refinery. N. Horton and W. Kolar. *Oil Gas J.*, 17.11.49, **48** (28), 72.—Modifications to the above refinery involving the desulphurization, thermofor, catalytic cracking TCC gas-recovery, and liquid Penco sweetening units are described.

The modifications which centre round the installation of a new 30,000-b.d. crude-oil distillation unit increase the plant's capacity to 52,500 brl of crude oil per day.

Storage facilities, including spheres for butane, have also been increased.

G. A. C.

265. Commercial desalting unit employing fiberglass as contacting agent. J. C. Hayes, L. A. Hayes, and H. S. Wood. *Chem. Engng Prog.*, 1949, **45** (4), 235–40.—The necessity of removing inorganic salts from crude petroleum prior to refining is remarked, and existing processes are briefly described. The development of a new process is outlined in which fine glass fibres are used as the contacting agent in the solid-contact method. Steps involved in the process comprise washing the crude oil with fresh water, heating the resulting emulsion to 200° F, coalescing the emulsified water by passing through beds of glass fibres, and separating the desalted oil from the water. Results over a year's operation are presented with the original glass fibres in service; during this period over 80% of the salt was consistently removed, with a max figure of 94% removal. J. G. H.

266. Heat transfer and pressure drop in heat exchangers. D. A. Donohue. *Industr. Engng Chem.*, 1949, **41** (11), 2499–511.—Development of a correlation of H.T.C. in unbaffled shells from the published experimental data results in a correlation different from that at present used. For a baffled shell H.T.C. is expressed by

$$\frac{hD}{k} = C \left(\frac{DG_s}{\mu}\right)^{0.6} \left(\frac{c\mu}{k}\right)^{0.33} \left(\frac{\mu}{\mu_w}\right)^{0.14}$$

where G_e is geometric mean of mass velocity across tube bundle and through baffle opening. While G_e allows for baffle spacing and size of opening, C accounts for structural characteristics—viz., arrangement of tubes within the shell and leakage areas. Values of C from the present data appear to be fairly constant for a given type of exchanger. Pressure-drop tests indicate partial flow penetration of the tube bundle. The effect of this partial penetration on H.T.C. and friction factor is discussed. Relation of H.T.C. and friction factor is noted. Disc-and-doughnut baffles produced higher H.T.C.'s than segmental baffles for corresponding values of fluid flow and pressure drop. R. G. T.

267. New heat transfer medium. G. W. Tripp. *Engineer*, 1949, **188**, 453–4.—Alkylnaphthalene (one of the fractions to be derived from the aromatic cracking units of Petrochemicals, Ltd.) can be suitably refined to a stable heat-transfer medium having applications similar to those of Dowtherm. It has a ceiling service temp of 600° F. and a f.p. $<14°$ F, as compared with 700° and 54° F respectively for Dowtherm. Its price will be well below that of Dowtherm, the latter being imported in any case from the U.S.A. Alkylnaphthalene has been in continuous use in an industrial fatty alcohol dist unit at 540° F for three years without noticeable deterioration in performance. A. C.

268. Transfer of heat and mass between air and water in a packed tower. W. H. McAdams, J. B. Pohlenz, and R. C. St. John. *Chem. Engng Prog.*, 1949, **45** (4), 241–52.—The objective of testing the basic equations for the simultaneous transfer of heat and mass between air and liq water was effected by designing a packed tower suitable for measuring the individual coeff and correlating the results. It was concluded that an overall coeff of enthalpy transfer should only be used with caution; the methods employed present a more logical means of designing and evaluating the performance of cooling towers. J. G. H.

269. Insulation of Socony-Vacuum's new lube-oil installation. Anon. *Oil Gas J.*, 24.11.49, **48** (29), 112.—The methods used for insulating the equipment of the new lub.-oil plant at the Paulsboro', N.J., refinery of the Socony-Vacuum Co. are described.

Thickness of insulation used is listed in a table, and protection or temp control, location of equipment, operating temp, and cost of heat production were taken into account.

Insulation ends cutting on to uninsulated areas were cement sealed and made weather-tight with asphaltic-asbestos plastic. G. A. C.

270. Maintenance of pumps for handling light volatile liquids. Anon. *Mech. World*, 4.11.49, **126** (3277), 533.—Use of sealing-oil systems on pump lantern-rings is quite common where packing has only to hold sealing oil in ring. Whatever packing is used for other rings it is advisable to place metallic packing on each side of lantern ring. A selected light lub. oil is preferable for sealing liquid except for dead-end system, when steam-cylinder oil is frequently employed. While a high-viscosity sealing oil is preferable, the actual viscosity depends on how much contamination of pumped liquid can be tolerated, at least to some degree. The paper discusses in detail the various points connected with the maintenance of pumps which have to handle light, volatile liquids. A. S.

Distillation.

271. Distillation column design for processing polymerizable compounds. K. E. Coulter. *Chem. Engng Prog.*, 1949, **45** (4), 227–34.—The design of dist columns handling polymerizable compounds is discussed with special reference to polymerization rates. Operating conditions are outlined, and questions of reboiler design, column-cleaning, conc gradients, and instrumentation are considered. J. G. H.

272. Maysville central processing plant. Anon. *Oil Gas J.*, 24.11.49, **48** (29), 91.—The plant includes compressor, absorber, complete distillation and fractionation units, storage, and loading facilities for gasoline and liquefied petroleum-gas products recovered in the three absorbers.

About 520,000 gal of mineral seal oil were required to fill the circulating system and

absorbers in the three interconnected units together with the heating-oil system and spare storage at Maysville.

Pressure storage at a capacity of 1,900,000 gal is provided for temporary storage of products.

A flow sheet illustrates the article. G. A. C.

273. Multicomponent rectification ; calculation on theoretical trays under conditions of variable molal overflow. D. S. Sherwin. *Chem. Engng Prog.*, 1949, **45** (5), 342–8.—A method is presented for the computation of the effects of varying internal liq and vapour rates on the number of plates of a dist unit. The method proposed depends first on the approximation that the molar enthalpy of the liq falling into a given tray is not affected greatly by the different trial assumptions for vapour rate from the given tray, and secondly, that the effects produced are small in comparison with the remaining enthalpies to be considered. J. G. H.

274. Separation of synthesis mixtures—phase equilibria in ethyl alcohol–ethyl acetate–water system. J. Griswold, P. L. Chu, and W. O. Winsauer. *Industr. Engng Chem.*, 1949, **41** (10), 2352–8.—The compounds of this ternary system are found in the water product of Fischer–Tropsch hydrocarbon synthesis. The present work presents supplementary vapour–liquid equilibria data on ethyl alcohol–ethyl acetate, liquid–liquid, and vapour–liquid equilibria of ethyl acetate–water, and of the ternary system. The liquid–liquid data are sufficiently complete between 15° and 70° C for decantation recovery operations. In contradiction of previous reports there is no ternary azeotrope of fixed composition. R. G. T.

275. Separation of synthesis mixtures—vapour–liquid equilibria of acetone–methanol–water. J. Griswold and C. B. Burford. *Industr. Engng Chem.*, 1949, **41** (10), 2347–57.—Acetone and methanol are major components of water product obtained from the Fischer–Tropsch synthesis. Vapour–liquid equilibria and b.p.'s of the acetone–methanol–water ternary mixture are presented. The present data resolve discrepancies in the acetone–methanol system, and complete the ternary data. Densities, refractive indices, and b.p.'s of improved accuracy are shown for the ternary and all binaries. The density data are in good agreement with International Critical Table values, but refractive indices are appreciably lower than the literature values at high water concns. R. G. T.

276. Performance of stainless steel McMahon packing. A. W. Fisher and R. J. Bowen. *Chem. Engng Prog.*, 1949, **45** (6), 359–69.—Performance of McMahon packings of two sizes, fabricated from $\frac{3}{8}$-in and $\frac{1}{2}$-in squares of 80- and 60-mesh stainless-steel gauze respectively have been studied during fractionation tests with an adiabatic 4-in column, 10 ft high, using benzene–ethylene dichloride mixtures and conditions of total liq reflux. Detailed comparisons are drawn between these and $\frac{1}{2}$-in brass and Monel McMahon saddles and stainless-steel, triangular pyramidal Stedman packings, together with economic considerations. The qualities of the series of McMahon packings so far developed are evaluated. J. G. H.

Absorption and Adsorption.

277. Gas absorption ; mass transfer coefficients as function of liquid, gas rates, tower packing characteristics. L. E. Hutchings, L. F. Stutzman, and H. A. Koch. *Chem. Engng Prog.*, 1949, **45** (4), 253–68.—The effect of variables on the mass-transfer coefficients in gas absorption was studied in three absorption towers, packed with $\frac{3}{8}$-, $\frac{1}{2}$-, $\frac{3}{4}$-, and $1\frac{1}{4}$-in Raschig rings, using an acetone–air–water system under a wide range of conditions at atm pressure and room temp. Equations for gas-film-transfer coefficients were developed for Raschig rings and other packings. Liq film transfer coefficients were found to vary with the liq rate and to be independent of packing size and gas rates. J. C. H.

Cracking.

278. Esso operates world's largest fluid catalytic cracking unit. G. Weber. *Oil Gas J.*, 1.11.49, **48** (30), 58.—A short description of the 41,000 b.d. capacity catalytic cracking plant now operating at the Bayway refinery, Linden, N.J., of the Esso Standard Oil Company is given.

The plant operates on 36,000 brl of fresh feed and 5000 brl of cycle stock for stream day, and the unit's output is 23,400 brl of gasoline, 5900 brl of heating oil, and 6500 brl of other products including residual fuel, dry gas, L.P.G., and feed stocks for alcohol, polymerization and alkylation plants on the site. G. A. C.

279. Components of gasoline produced by catalytic cracking. A. R. Glasgow, Jr., C. B. Willingham, and F. D. Rossini. *Industr. Engng Chem.*, 1949, **41** (10), 2292–7.—A gasoline produced by a cat cracking process of the fixed-bed type of Houdry design was analysed with respect to individual hydrocarbon components. Analysis consisted of a combination of: (1) analytical distillation with measurements of b.p. and refractive indices of fractions; (2) separation of aromatic from naphthenic constituents by adsorption; (3) f.p., sulphur content, bromine absorption, and density determinations on the fractions produced by (1) and (2) and by further distillations of (2). Graphical and tabular results are included. R. G. T.

280. Coprecipitated chromia–alumina catalysts for naphtha reforming with hydrogen. E. C. Hughes, H. M. Stine, and S. M. Darling. *Industr. Engng Chem.*, 1949, **41** (10), 2184–8.—A coprecipitated chromia–Al_2O_3 cat was compared with published data of a molybdena–Al_2O_3 cat and found to show an equivalent performance. Preparation of the cat was carried out with careful control of pH during precipitation and of chromia–Al_2O_3 mol ratio. Cat properties claimed include resistance to high temp, water vapour, and organic S compounds. Moderate H_2 pressures result in higher liquid yield and decreased C laydown. Increased H_2 pressures had a repressive effect on the reactions. The dehydrocyclization was shown to proceed through an olefin intermediary, and the repressive effect of H_2 is probably due to reversal of the initial dehydrogenation. Differences between chromia and molybdena cats reported in the literature are suggested as due to the sensitivity of chromia cats towards H_2. R. G. T.

281. Application of contact coking to California refining. A. H. Schutte. *Oil Gas J.*, 3.11.49, **48** (26), 70.—A study of the effect of adding contact coking to the existing equipment in a typical California refinery is given.

Contact coking consists of applying a residual stock to a continuous stream of preheated coke particles produced in the process.

Correct adjustment of coke-to-oil ratio and the particle-size range of the circulating coke stream results in a free-flowing condition, thus allowing easy withdrawal of bed particles for reheating and recirculation to oil-contacting zone.

Comparisons of operating schemes are given, and a figure shows differential earnings versus price of fuel oil. G. A. C.

Alkylation.

282. Alkylation of *iso*butane with propylene—commercial production using sulphuric acid catalyst. E. C. Oden and W. J. Burch, Jr. *Industr. Engng Chem.*, 1949, **41** (11), 2524.—Alkylation of *iso*butane is described with an olefin feed varying from 0 to 100% propylene and 100–0% butylene and/or dimer. Horizontal, jet-type Kellogg-designed reactor settlers were used with H_2SO_4 as cat. Yields of 2–6000 b.d. of light alkylate were obtained. Variables affecting octane quality and acid consumption are assessed and typical distillation and combining ratio data for various product types are presented. Economic considerations depend on available raw materials and cheap regeneration of spent acid. Differential costs between raw material and alkylate, and cat costs are the basic economic factors. R. G. T.

283. Alkanesulphonic acids as catalysts in polymerization and alkylation. W. A. Proell and C. E. Adams. *Industr. Engng Chem.*, 1949, **41** (10), 2217–21.—The lower mol.wt. alkanesulphonic acids are effective cats for polymerization of olefins and alkylation of aromatics with olefins. Specific thermal conditions apply in each process. Ester formation between cat acid and olefin occurs at 0–60° C, and alkylation or polymerization at 60–150° C. The latter processes take place only at temps at which the esters become thermally unstable and not at all with olefins which do not form esters. It is therefore presumed that esters are essential intermediates in the process of alkylation and polymerization. Further advantages claimed for the use of

alkanesulphonic acids as cats include the absence of side-reactions such as hydrogen transfer, sulphonation, and formation of complexes. R. G. T.

Special Processes.

284. Separation of gas–oil and wax fractions of petroleum by adsorption. B. J. Mair, A. J. Sweetman, and F. D. Rossini. *Industr. Engng Chem.*, 1949, **41** (10), 2224–30.—Separation of gas–oil and wax fractions of pet has been carried out by adsorption with Si_1O_2 gel. The gas–oil fraction was separated, in a single-pass operation, into three parts—a mixture of paraffins and *cyclo*paraffins, one part of largely monomolecular aromatics and a third part of largely polynuclear aromatics. The wax fraction can similarly be separated into two parts—one of paraffins and the other of *cyclo*paraffins. Several of the factors affecting the separation of gas–oil have been studied, and data are supplied. The authors draw a simple analogy between fractionation by adsorption and by distillation. R. G. T.

285. Fischer–Tropsch synthesis—differential reaction rate studies with cobalt catalyst. R. B. Anderson, A. Krieg, R. A. Friedel, and L. S. Mason. *Industr. Engng Chem.*, 1949, **41** (10), 2189–97.—A study of reaction rate for the Fischer–Tropsch synthesis has been made using cobalt cats at atm pressure. Synthesis rate was high in the first part of the bed, and lower and nearly constant throughout a large part of the cat bed until nearly 100% of reactants had been consumed. Gas composition was found to vary considerably over the constant-synthesis-rate range. CH_4 and CO_2 are primary products, CH_4 is also a secondary product of cracking of high-mol.-wt. hydrocarbons and CO_2 in the water-gas reaction. The latter reactions occurred throughout the bed, and depended on composition of the gas. Craxford's postulates are discussed—involving synthesis on cobalt carbide and secondary reaction on cobalt atoms. They do not adequately explain the present data. R. G. T.

286. Synthetic gasoline from natural gas (composition and quality). F. M. Bruner. *Industr. Engng Chem.*, 1949, **41** (11), 2511–75.—Comparison is made between gasoline produced by fluidized iron-catalyzed hydrogenation of CO and by Fischer–Tropsch fixed-bed, Co-catalyzed processes. The former produces low-boiling, highly olefinic products; the latter, high-boiling paraffinic materials. Olefins in the former product are straight-chain or monomethyl with double bond in 1-position. Single cat treatment produced high-octane fuel or blending stock for straight-run and cracked products. R. G. T.

287. From synthetic fuels, what chemicals? P. W. Sherwood. *Chem. Engng*, 1949, **56** (9), 99–101.—Increased liquid-fuel production will involve simultaneous production and recovery of important basic chemicals which will affect markets. Shale dist, high-pressure hydrogenation, and Fischer–Tropsch synthesis produce a variety of products. Fischer–Tropsch gives straight-chain paraffins and olefins, high-mol.-wt. waxes, fatty acids for detergents and plasticizers, alcohols, ketones, aldehydes, and esters. Coal hydrogenation yields phenols, cresols, xylenols, and other tar acids and bases such as pyridine; secondary chemicals include acetone, methyl ethyl ketone, acetonitrile, and smaller percentages of coronene, pyrene, and carbazole. From shale oil are derived ammonia, phenol, cresol, pyridine, and other bases, picoline, lutidines, quinoline, etc., and small amounts of ethylamine and diethylamine. R. G. T.

Metering and Control.

288. Automatic boiler control. R. Hammond. *Chem. Prod.*, Dec. 1949, **13** (1), 12.—Various control systems are described, and, while it is emphasized that none of them can be expected to operate satisfactorily without efficient and frequent maintenance, a preference is expressed for hydraulic control mechanisms. O. M.

289. New method measures the solid : gas ratio in high solid flow. J. M. Dotson, J. H. Holden, C. B. Seibert, H. P. Simons, and E. D. Schmidt. *Chem. Engng*, 1949, **56** (10), 129–30.—Studies on flow of extremely dense coal–air mixtures, to devise a method for ensuring constant rate of coal feed led to development of electronic method

for measurement of instantaneous solid : gas flow through a tube when solid occupies 20% by vol. A charge of 0·1 vol % of solids can be detected. R. G. T.

290. The critical flow of superheated steam through nozzles. J. R. Finniecome. *Mech. World*, 2.12.49, **126** (3281), 649.—A simple expression is given which assists the quick and accurate determination of the critical flow of superheated steam through nozzles at pressures from 0 to 300 lb/sq. in. In previous articles a series of graphs on the critical flow factor for pressures up to 2000 lb/sq. in. were presented. As a large number of industrial plants operate below 300 lb/sq. in. a series of curves are presented in this paper on the critical flow factor for a range of pressures from 0 to 300 lb/sq. in. and for temperatures up to 800° F. A. S.

Safety Precautions.

291. The handling of leaded gasoline. M. A. Pryke. *I.P. Review*, 1949, **3**, 321.—Gasoline itself has detrimental effects when inhaled or when brought into contact with skin and particularly with the eyes. The addition of T.E.L. to improve the " anti-knock " properties naturally aggravates the dangers, due to the high toxicity of the volatile lead compound. When used in motor spirit the maximum vol conc of ethyl fluid allowed is 1 : 1260. Hazards are mainly experienced by refinery personnel in carrying out filling, dipping, and cleaning operations. The safeguards are careful handling, adequate ventilation, and the use of protective clothing where appropriate. Other less dangerous situations are those encountered in testing and overhaul of engines, handling of containers, and work with pipelines. A general rule to be observed is that gasoline should never be used other than in petrol engines. R. H.

292. Industrial protection against the effects of sulphur dioxide. Anon. *Mech. World*, 25.11.49, **126** (3280), 614.—In industry sulphur dioxide is formed as a by-product of a great number of processes. In sufficient conc it may cause damage to vegetation, and its toxic action on humans is as a lung and skin irritant. It produces a detectable odour at a concn of 3–5 parts per million of air and higher concn (20 p.p.m.) produce irritation of eyes and coughing. Repeated exposure to significant quantities of the gas may result in a number of diseases and concn of 400–500 p.p.m. are dangerous even for short exposures. In any industrial operation where sulphur dioxide is not confined to a closed system, air tests should be conducted and the degree of atm contamination ascertained. Where the concn of the gas exceeds the max allowable concn, protection should be provided by means of exhaust ventilation systems, approved respirators, or air-line respirators. Instruction on the use of protective equipment should form part of employee training. A. S.

293. Radar keeps tab on tropical storms. W. F. Gordes and R. C. Jorgensen. *Oil Gas J.*, 17.11.49, **48** (28), 76.—An account is given of how radar works, and its application to the tracking of tropical storms, together with installation details of radar equipment. When a hurricane is predicted, equipment in its path can be shut down for fear of wind damage.

A test of the system was provided by the Gulf (U.S.A.) hurricane of Oct. 2–4, 1949, which was tracked by radar and described in the article, which is also illustrated by seven figures. G. A. C.

Products.

Chemistry and Physics.

294. Low temperature vapor–liquid equilibrium : 2. equilibrium constants for nitrogen, methane, and ethane at low temperatures. G. M. Brown and L. F. Stutzman. *Chem. Engng Prog.*, 1949, **45** (2), 142–8.—Equilibrium vaporization constants for nitrogen, methane, and ethane are presented for the temperature range −360° to 240° F and for pressure up to 1000 p.s.i. abs. These correlations are presented in the form of simple equations, and are reasonably accurate for pressures below 0·2 times the convergence pressure. A comprehensive bibliography and compilation of experimental data are included. J. G. H.

295. Vibration spectra of hydrocarbon molecules. II. Skeletal frequencies in certain branched paraffins. D. M. Simpson and G. B. B. M. Sutherland. *Proc. Roy. Soc.* A, 1949, **199** (1057), 169–83.—Saturated paraffins containing the terminal grouping $(CH_3)_2C$. . . show strong absorption bands in the infra-red at 1250 and 1200 cm^{-1}, while those containing the terminal grouping $(CH_3)_2CH$. . . show strong bands at 1170 and 1145 cm^{-1}. It has been shown that these and other characteristic frequencies should be assigned as vibrations of the carbon skeleton of these structural units. Further, by using a simple valency force field on the model molecules X_3YZ and X_2WZ (where X is a CH_3 group, Y a carbon atom, W a CH group, and Z a large mass representing the remainder of the molecule), satisfactory agreement between observed and calculated frequencies is obtained. The implications of these results in the more general problem of the interpretation of the vibration spectra of hydrocarbons is considered. In particular, it is emphasized that such skeletal frequencies are at least partly responsible for the intense and complex absorption spectra of branched paraffins, in the interpretation of which stress has hitherto been placed mainly on the role of vibrations of the hydrogen atoms. W. H. C.

296. Fluorescence spectra of anthracene, 1 : 2-benzanthracene and some of their derivatives. E. V. Shpol'skii, A. A. Il'ina, and V. V. Bazilevich. *Doklad. Akad. Nauk S.S.S.R.*, 1948, **62**, 227–30.—Fluorescence was excited by light from an Hg lamp filtered at 3650 Å. The test substances were dissolved (10^{-3} to 10^{-4} g/ml) in benzene and in white medicinal oil. Curves showing fluorescence intensity (measured photoelectrically) against wavelengths (3800–4800 Å) are given for nine compounds. Certain preliminary conclusions regarding the effect of substitution in the anthracene mol on fluorescence spectra are made; apart from other changes displacement of the spectrum towards longer wavelengths occurs. V. B.

297. Infra-red absorption spectra of the liquid butenes and 1 : 3-butadiene. E. C. Creitz and F. A. Smith. *Bur. Stand. J. Res., Wash.*, Oct. 1949, **43** (4), 365.—The infra-red absorption spectra from 1 to 15μ, of 1-butene, 2-methylpropene (*iso*butene), *cis*-2-butene, *trans*-2-butene, and 1 : 3-butadiene have been recorded in the liq phase under pressures high enough to liquefy them at room temp. The spectra of the same samples in the vapour phase have been recorded, and are presented for comparison. The spectra of the five samples were recorded in the liq phase from 2 to 15 μ with a rock-salt prism and from 1 to 4·2 μ with a lithium-fluoride prism. The spectra obtained from the liq phase provided data for the development of a procedure for the analysis of liq plant streams by spectrometric methods. A. S.

298. Ethane pyrolysis. H. J. Hepp, F. P. Spessard, and J. H. Randall. *Industr. Engng Chem.*, 1949, **41** (11), 2531–4.—Pyrolysis of ethane in copper-lines alloy steel tube at temps between 1700° and 1900° F is described. H_2 and C_2H_4 are major products, with appreciable C_2H_2 and butadiene. C_2H_4 increased with temp to 37% at 180° F. C_2H_2 increased similarly to 3·4% at highest temps used. Butadiene reached steady state of 1%. H_2, CH_4, and $C_2H_4 + C_2H_2$ are related to temp, pressure, and reaction time on basis of equilibrium dissociation of C_2H_4. First-order-velocities consts lie on extrapolated Steacie–Shane C_2H_6 rate equation. R. G. T.

299. Sulpho-chlorination of Kogasin in the dark. H. Kroepelin, W. Opitz, and W. Freiss. *Erdöl u. Kohle*, 1949, **2**, 498–500.—Tests on the reaction of Kogasin (boiling range 225–305° C) with Cl_2 and SO_2 were made, using Kogasin of three grades of purity, "technical," "refined" (olefin-free), and a super-refined material (olefin-free vac dist over Na in N_2). Using the "refined" material, chlorination was the main reaction at 25–38° C and sulpho-chlorination at 38–68° C (temp measured in reaction vessel). The best ratio between chlorination and sulpho-chlorination was at 68° C. "Technical" Kogasin reacted similarly but somewhat more energetically. Using the highly refined Kogasin, reaction with $Cl_2 + SO_2$ could not be obtained. In the course of analyses of the Kogasins marked sensitivity of the refined olefin-free material to O_2 was observed in the temp range 100–130° C. Tests with the most highly refined material, to which 0·5% of chain initiators (dodecylene-1, benzoyl peroxide) had been added showed strong combination with Cl_2 and SO_2 at temp of 71–77° C, the products containing approx 16% Cl and 9% S. Inhibitors of the reaction (*e.g.*, alcohols, pyri-

dine) were also tested ; in the case of pyridine the inhibitory action is due to a pyridine–chlorine compound. Smooth sulpho-chlorination of pet fractions from crude oil was not obtained, presumably due to the presence of natural inhibitors. The experiments confirm that, even in the dark, sulpho-chlorination is a chain reaction. V. B.

300. Reaction of nitrogen atoms with ethylene. J. H. Greenblatt and C. A. Winkler. *Canad. J. Res.*, 1949, **27B** (8), 721–31.—Reaction products are hydrogen cyanide, ethane, and a polymerizable material. Yield of HCN is *ca* 70% of the ethylene consumed by nitrogen atoms, while the amount of polymerizable material averages *ca* 16% by wt of the HCN produced. The yield of ethane increases as the excess of ethylene over nitrogen atoms is increased. An activation energy of 6·9 k.cal is calc from collision yields, a steric factor of 0·1 being assumed. The mechanism proposed for the reaction involves rupture of the ethylene double bond with the formation of HCN and a methyl radical, the latter then reacting with nitrogen atoms. D. F. J.

301. Application of the diffusion flame technique to the reaction between nitrogen atoms and ethylene. J. H. Greenblatt and C. A. Winkler. *Canad. J. Res.*, 1949, **27B** (8), 732–7.—Rate constants for the reaction between nitrogen atoms and ethylene have been obtained by diffusion-flame technique over the temp range 273–373° C. An activation energy of *ca* 3 k.cal has been obtained from the temp coeff of these rate constants, and using this value a steric factor of 10^{-2} has been obtained. The difference between the activation energy calc by this method and that obtained in a previous study (see Abstract No. 300) is discussed. D. F. J.

302. Effect of phosgene upon the inflammability limits of hexane. K. J. McCallum and H. M. Trainor. *Canad. J. Res.*, 1949, **27B** (5), 409–11.—The investigation was made at approx atm pressure. The addition of phosgene causes the upper and lower inflammability limits of hexane to approach each other until they meet at a composition of 3·4 vol % hexane and 19·1 vol % phosgene. D. F. J.

303. Hydrogen of *cyclo*pentane in presence of nickel and of palladium. B. A. Kazanskii and T. F. Bulanova. *Doklad. Akad. Nauk S.S.S.R.*, 1948, **62**, 83–6.—Hydrogenation of *cyclo*pentane using Ni on Kieselguhr and space velocity 0·5–0·6 was carried out at 200°, 250°, and 300° C. There was no reaction at 200°, at 250° 29%, and at 300° 34% of the *cyclo*pentane was converted to CH_4. At the latter temp the liq product contained 4% *n*-pentane and 7% of aromatics (unidentified). Using Pd cat there was no reaction at temp up to 300°. These results confirm earlier findings that platinized charcoal, which reduces *cyclo*pentane to *n*-pentane, is a specific cat for this reaction. V. B.

304. Mercury photosensitized reactions of *neo*pentane. B. de B. Darwent and E. W. R. Steacie. *Canad. J. Res.*, 1949, **27B** (4), 181–9.—The investigations were carried out between 50 and 400 mm Hg and between 25° and 200° C in the presence and absence of H_2. The products are mainly H_2 and dineopentyl. Reaction mechanisms are discussed. D. F. J.

305. The pyrolysis of methane, ethane, and *n*-butane on a platinum filament. A. J. B. Robertson. *Proc. Roy. Soc.*, A., 1949, **199** (1058), 394–410.—At a pressure of the order of 10^{-5} the nature of the reactions of methane, ethane, and *n*-butane on an incandescent platinum filament were determined by means of a mass spectrometer. The general arrangement of the apparatus used is shown and described.

The free radicals evolved were detected by ionizing them with low-energy electrons.

In the primary dissociation of methane on platinum at *ca* 1000° C methyl radicals were found but no methylene radicals. About 1 in 300 collisions of the methyl on the platinum led to reaction. Further reactions of radical recombination and hydrogen transfer produced ethane, propane, and butane, and part of the ethane was dehydrogenated on the platinum to ethylene. The extent of dehydrogenation was the same as that found with pure ethane.

In the dehydrogenation of ethane to ethylene at 950° C no free methyl or ethyl radicals were detected. Methane and higher hydrocarbons were not formed. This reaction is considered to be a molecular dehydrogenation.

In the products of pyrolysis of *n*-butane at 1050° C ethyl radicals were present,

The main constituents were ethane and ethylene and traces of: (1) unidentified higher hydrocarbons, and (2) methane were observed. No C_2 hydrocarbons were detected. Thus the butane underwent a selective fission at the central carbon–carbon bond. Consideration of bond dissociation energies in butane shows that this selective fission very probably arises from the influence of the platinum catalyst, and not from a property of the butane itself. W. H. C.

306. Tetranitromethane. K. F. Hager. *Industr. Engng Chem.*, 1949, **41** (10), 2168–72.—Tetranitromethane is of theoretical interest for its configuration and formation of coloured complexes with double bonds, and of practical interest as an intermediate to form nitroform (trinitromethane), as a mild nitrating agent less corrosive than nitric acid, as a highly explosive mixture with hydrocarbons, as an O_2 carrier of high sp. gr., and in its ability to increase the cetane No. of diesel fuel. A technical method is suggested for its manufacture, based on work done in laboratory apparatus with capacity up to 14 kg/day. R. G. T.

307. Specific heat of napalm-gasoline gels. G. O. Langstroth and K. H. Hart. *Canad. J. Res.*, 1949, **27A** (4), 151–5.—The heat capacities of gasoline, napalm, and various napalm-gasoline gels have been measured in the temp range −50° to 50° C by the method of mixtures using an ordinary type of Richards adiabatic calorimeter. Within this range of temp, the specific heat (S_T) in cals/gm/° C at T° C is given to within 2% by

$$S_T = 0{\cdot}479 - 0{\cdot}00054\ C + 0{\cdot}00092\ T$$

where c = napalm concn in wt % D. F. J.

308. Significance of properties of petroleum products: V. Oxidation and oxidation stability. D. L. Samuel. *I.P. Review*, 1949, **3**, 325.—All petroleum products undergo some form of oxidn when stored, exposed, or used. The rate of oxidn is greatest for gasoline and least for bitumen, and little is known about the course of the reactions. Various methods are used for determining the stability to oxidn of gasoline and lub. oils, including engine tests. No method is, in general, used for bitumen. The production of gum and acids in gasoline and lub. oil respectively detracts from satisfactory performance, and refinery processes are used to eliminate these undesirable properties. R. H.

309. Mixture law for viscosity. L. Grunberg and A. H. Nissan. *Nature*, 1949, **164**, 799.—The Arrhenius equation for the viscosity of a solution can be modified to: $\log \eta_s = N_1 \log \eta_1 + N_2 \log \eta_2 + N_1 N_2 d$, where η is the viscosity, N is the mole fraction, and the subscripts 1, 2, and s refer to the two components and the solution. d is a constant characteristic of the system, and has a +ve or −ve value for systems showing −ve or +ve deviations from Raoult's Law. $d = b \log \eta / \log$ vapour pressure, where b is the constant in the simplified Margules equation: $\log \gamma_1 = bN_2^2$, γ_1 being the activity coefficient of component 1. Results are given for the system *trans*-decalin/*cis*decalin. H. C. E.

310. On a complete solution of the one-dimensional flow equations of a viscous, heat-conducting, compressible gas. M. Morduchow and P. A. Libby. *J. Aero. Sci.*, 1949, **16**, 674.—The hydrodynamic equations describing the steady, one-dimensional flow of a visc, heat-conducting, compressible gas are treated. The equation of state for a perfect gas is assumed valid, and the coeff of specific heat are assumed constant. A complete integral of the energy equation is found for a Prandtl Number of $\frac{3}{4}$, which is a good approx for the actual value of many gases over wide temperature ranges. A particular integral contained in this complete integral is $(u^2/2) + c_p T = a$ constant, which is a frequently used one-dimensional energy equation. The restrictions on its use are rigously derived and stated. With the complete integral of the energy equation, three different types of solutions which depend on the boundary conditions are shown to be obtainable. The usual shock-wave solution (satisfying the Rankine–Hugoniot relations) is only one of these three types. I. G. B.

311. Effect of oil on plastic properties of petroleum waxes—development of plasticity tests. W. L. Nelson and L. D. Stewart. *Industr. Engng Chem.*, 1949, **41** (10), 2231–8, —The effect of oil on the properties of pet wax, particularly microcrystalline waxes,

has been studied. Blends of white oil with typical waxes were tested for m.p., penetration, crystallinity index, plastic point, ductility, tensile strength, compressive strength, and flexibility. Several of the test methods were only modifications of the standard methods. Flexibility was determined by bending a wax stick until rupture occurred. Compressive strength was a better criterion than tensile strength. Paraffin wax is affected by solution of some wax by oil entering the space between interlocking crystals. Microcrystalline waxes are gradually affected by dilution of the continuous phase which alters the wax properties and may precipitate additional microcrystals. Oil is not found to improve the plasticity or flexibility of wax except with extremely hard or high m.p. microcrystalline waxes. R. G. T.

312. Rheological measurements and adhesion. J. F. T. Blott and W. B. Bonner. *Nature*, 1949, **164**, 799.—In measuring yield stresses in lub. greases under conditions of simple tangential shear, flow of grease took place by slip of a thin oil film at the grease–solid interface above a certain shearing stress (" first yield stress "). At higher stresses (" second yield stress ") flow occurred as a result of breakdown of grease structure, and this is the yield value commonly measured. Theoretical reasons for the " first yield stress " are advanced. Since stresses of this type occur at interfaces, whereas " second yield stresses " occur in the bulk grease, the effect of surface might be expected to show at stresses intermediate between the former two; and in fact Mardles' experiments (Abs. No. 1815, 1949) show that this is the case. H. C. E.

313. Vapour pressures, viscosities, surface tensions, and equilibrium proportions of ideal mixtures. M. Roegiers. *Chim. et Ind.*, 1949, **62**, 466–7.—A summary is given of a paper the full text of which is obtainable from the author. Theoretical considerations concerning ideal mixtures are developed, and applying these to binary mixtures it is possible, from a knowledge of the visc of the two components and of a known mixture thereof, to calculate isothermic curves relating visc to mixture composition and also relating the proportions of the mixture in the gaseous and liquid phases. Pet fractions which are Newtonian fluids and which have been refined to remove polar components are normal fluids to which such rules apply. Experimental verification of the theories developed has been made for binary mixtures composed of liquids of widely varying visc (gasoline + bright stock). V. B.

Analysis and Testing.

314. Estimation of Epoxides. G. King. *Nature*, 1949, **164**, 706.—Epoxides react smoothly and quantitatively with HCl in dry ethereal solution, and can be estimated by this means. It is found that similar results can be obtained by employing 1–1·5% conc HCl in pure dioxan. For the estimation about 0·1 g epoxide-containing material is reacted with 10 ml of dioxan/HCl solution, and after 10 min the solution is titrated against N/10 sodium hydroxide to determine the residual acid. A blank estimation is made simultaneously. The method yields results between 96 and 99% of theoretical values. H. C. E.

315. Effect of exposure. J. K. Long. *Brit. Plastics*, Nov. 1949, **21** (246), 590.—Results of a comprehensive series of outdoor-exposure tests on flat sheets of thermoplastic materials and also of various laminated products are described. It was noted that accelerated weathering tests correlated with the outdoor tests in respect of flexural strength and flexural modulus of elasticity in the case of cotton-fabric base urea–phenol–formaldehyde laminated, but not with ethyl cellulose sheet. Wet strength after 24 hr immersion in water showed no general correlation with strength after outdoor exposure. None of the panels was seriously damaged in appearance by exposure. O. M.

316. Instruments for testing paints. N. R. Fisk. *Paint Technol.*, Nov. 1949, **14** (167), 511.—A brief review of paint-testing instruments developed by Eben E. Jelpke, under the general name of "Sheen," is presented. Subjects discussed include: the Mobilometer, Glossometer, Bend Test Instrument (made in mandrel sizes from $\frac{1}{8}$ to 1 in), the Scratch Test and needles, Hardness Rocker, Film Applicator, and " Lab Dip," Wet Film Thickness Gauge, and measurement of Drying Time.

1-mm spheres can be welded on to a steel rod in the production of ball-ended needles for the scratch test. Other needles are tipped with tungsten carbide.

The Wet Film Thickness gauge consists of a small, heavy brass wheel about ½ lb in weight and 2 in in dia. The rim has two narrow ridges on the outside on an inner wider ridge mounted eccentrically, level at zero and 4/1000 in less in dia than the outer ridges; this represents the thickest film that can be measured. D. K.

317. Laboratory fractionation-column head. K. W. Schneider and C. Schmid. *Erdöl. u. Kohle*, 1949, **2**, 508–10.—A detailed description and diagram are given of an all-glass column head utilizing total condensation and suitable for columns handling up to 1500 ml/hr. At this latter rate hold-up in the head is 2 ml. Reflux ratio is controlled by a drop-counter (details shown) suitable for quantities up to 400 ml/hr; a modified form for higher distillation rates is also available. The No. of drops/ml (25–30) given by this counter is substantially similar for gasoline and spindle oil. V. B.

318. Standardization of acid with potassium iodate. P. Oesper. *Chem. Education*, Nov. 1949, **26** (11), 588.—Potassium iodate has none of drawbacks involved with use of most of the common primary standards for acidimetry. It is not hygroscopic, and its solutions are indefinitely stable. An indicator should be used with an end point distinctly on the acid side, such as methyl yellow. It is then possible to titrate directly to the end point (pH 3·5). Alternatively an indicator like methyl red, which changes colour at pH 5, may be used; it is then necessary to wait several minutes for reaction to go to completion, and to add more acid should colour revert to alkaline shade as last traces of iodate react. Either procedure is satisfactory when acid is 0·1N or stronger, but difficulties arise in titrating with weaker solutions. These difficulties can be overcome by use of a mixed indicator, which has a much sharper colour change than a single indicator, and by addition of large excess of potassium iodide, which accelerates the reaction sufficiently, even at pH 5, to make it possible to carry out titration with only a few minutes' waiting at end point. Since thiosulphate also catalyzes reaction, an excess of thiosulphate is a distinct advantage in titration with acid more dilute than 0·05N. Paper describes procedure which is quite accurate for standardization of strong acids whose concentration is 0·01N or more. A. S.

319. Automatic titration demonstration. W. S. DeLoach, J. L. Eiland, and J. G. Harmon. *Chem. Education*, Nov. 1949, **26** (11), 609.—The paper described an "Automatic titration" apparatus recently displayed in the chemistry department of Huntingdon College at a Science Open House. The apparatus was so arranged as to deliver alternately a small amount (5 or 6 drops) of IN-NaOH and of IN-H_2SO_4 into a 1-litre beaker containing 600 or 700 ml of distilled water plus 2 or 3 ml of phenolphthalein solution. Contents of the beaker were stirred by electric motor. Acid and base were delivered by siphon into reaction beaker. The siphons were alternatively opened and closed by having part of each made of rubber tubing so that one could be pulled down and pinched shut while other was pulled up and held open. The alternate raising and lowering were effected by attaching the rubber tubing of siphons to opposite ends of a rocker operated by water power. The paper gives a diagram illustrating the set-up and also a complete description of the operation. A. S.

320. Viscometer for determining the viscosity of oils under pressure. V. M. Fokeev. *Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk*, 1949, 1334–42.—A falling-sphere viscometer suitable for visc of 0·002 to 50 poises and pressures up to 300 atm in the temp range 20–60° C is described. The viscometer is a heavy-walled stainless-steel cylinder connected to a pump by a spiral (4·5 m) Cu tube. The capacity of the system is 50 ml. Release of ball and timing of its fall (vertical) are done electrically. For the lowest visc (0·002 poise) time of fall is 1·14 sec, which can be determined to about ±3%. Reynolds No. governing the fall in a typical low-visc material showed this to be 0·03–11·3, well within the limits of laminar flow. Spheres used had dia 5·5 and 10·3 mm with tube dia of 12·5 and 11·0 mm respectively. Ht of fall was 170 mm. V. B.

321. Viscometer for thick liquids. Anon. *Brit. Plastics*, Nov. 1949, **21** (246), 590.—This instrument has been developed for the examination of materials which are volatile,

sticky, and opaque, and which may or may not obey the Newtonian law. In it a constant air pressure forces the liq under test into a horizontal glass capillary tube graduated so that the visc is numerically equal to a simple multiple of the time taken for the meniscus of the liquid to pass from one mark to the other. The constant pressure is produced by what is essentially a dead-weight gauge operating under conditions of low friction. By the instrument, visc is measured in absolute units (poises). O. M.

Crude Oil.

322. Refining crude in western Canada. Imperial Oil Ltd. *Oil Gas J.*, 3.11.49, **48** (26), 77.—Characteristic analysis of recently discovered Canadian crudes is given, and the economic effects of the field's development on Canadian economy discussed.

Tables show true-boiling-point assays of distillate light gas oil, lub.-oil distillate, and bottoms products.

It is thought that high-quality lub. oils can be produced from the Leduc crude with conventional extraction and de-waxing processes. G. A. C.

323. Elementary composition of petroleum ashes. S. M. Katchenkov. *Doklad. Akad. Nauk S.S.S.R.*, 1948, **62**, 361–3.—Spectrographic examination was made of ashes from crudes from fifty-four wells in various parts of the U.S.S.R. Ash was obtained by decanting crude from any accompanying water, washing it with dist water, filtering, evaporating, and igniting the residue at 700° C. Quant results are given in five groups: 3% and over, 1–3%, 0·1–1%, 0·01–0·1%, and 0·001–0·01%; qual findings cover thirty-two elements. All ashes examined contained Ca, Mg, Na, Al, V, Fe, Ni, Cu Sr, Mn, Ba, Si. In no case could Ag, Au, As, Cd, and Zn be found, although such elements had previously been reported in pet ashes. The increase in V content with age of crude is confirmed, and an inverse relationship between age of oil and Sr content established, this being in ratio 1 : 3 : 6 : 9 for crudes from Devonian, Carboniferous, Jura limestone, and Tertiary deposits respectively. V. B.

324. Mercaptans from Ishimbaevsk petroleum. S. S. Nametkin and A. S. Sosnina. *Doklad. Akad. Nauk S.S.S.R.*, 1948, **62**, 775–8.—Fraction from crude, up to 200° C, was re-fractionated, and five cuts (80–120°, 120–125°, 125–130°, 130–132°, and 135–137°) with high (0·92–1·21%) S contents examined. The isatin test for thiophene was neg in all cases. By treatment with a saturated aq solution of $HgCl_2$ followed by purification of the resultant precipitates by extraction with Et_2O and EtOH and subsequent decomposition of the Hg salt with HCl, *sec*-butyl mercaptan, and *n*-amyl mercaptan were isolated and identified. Two other compounds, which were almost certainly *iso*amyl mercaptan and hexyl mercaptan, were also obtained. V. B.

325. Sulphides from Ishimbaevsk petroleum. S. S. Nametkin and A. S. Sosnina. *Doklad. Akad. Nauk S.S.S.R.*, 1948, **63**, 391–4.—Treatment of fractions of b.p. >140° C with $HgCl_2$, as previously carried out for separation of mercaptans (see Abstract No. 324/1950), results in separation of aliphatic and cyclic sulphides in the form of addition compounds with $HgCl_2$. Such compounds were purified by extraction with EtOH, decomposed with HCl, and the resultant material further purified by dist. From the 145–149° cut dipropyl sulphide was obtained (m.p. of $(C_3H_7)_2S.2HgCl_2$, 130–131°). A cyclic sulphide $C_6H_{12}S$, probably hexylthiophane was isolated from a crude fraction with b.p. <140°; from the 142–143° fraction an isomer, probably dimethyltetramethylene sulphide was obtained. Heptyl thiophane and *iso*-octyl thiophane were isolated, and identified with reasonable certainty, from the 145–149° and 106–108° (50 mm) fractions respectively, the presence of nonyl thiophane in the latter was indicated. V. B.

Gas.

326. Natural gas from Saint-Marcet and its utilization. G. Genin. *Chim. et Ind.*, 1949, **62**, 503–9.—Production of gas from the Saint-Marcet field has risen from 9 (1942) to 174 (1948) million m^3/year, and is scheduled to attain 1 million m^3/day. Reserves are estimated at 7×10^9 m^3. After removal of propane/butane fraction (approx 1750 tons/year) and natural gasoline (approx 7000 tons/year) the gas analyses (%)

CH_4 93, C_2H_6 3·8, C_2H_8 1, C_4H_{10} 0·2, N_2 3. For distribution as town gas it is planned to crack the gas in presence of steam over Ni cat followed by conversion over a second cat to yield a product having 76% H_2 and a cal. val. suitable for existent appliances. The desirable priorities of use, from the aspect of national economy, are : as town gas and automotive fuel, for manufacture of nitrogenous fertilizers, for chemical synthesis, and finally for industrial heating. Present $ saving is 7 million/year and will rise to 17 million/year at planned output of the field. V. B.

Engine Fuels.

327. Anti-knock quality requirements—high compression ratio passenger car engines. R. W. Scott, G. S. Tobias, and P. L. Haines. *Industr. Engng Chem.*, 1949, **41** (10), 2342–7.—Anti-knock studies employing the Borderline technique have been made on sixteen gasolines to determine the anti-knock quality requirements of high C.R. gasoline engines. Gasolines varied in composition, O.N., and T.E.L. content. C.R.'s of 8·0, 10, and 12·5 to 1 were used. Results show that anti-knock quality requirements of the engines in terms of laboratory O.N.'s may be expressed as a function of C.R. varying at sea-level from 92 research O.N. at 8 : 1 C.R. to 102 Research O.N. at 12·5 : 1 C.R. In high C.R. engines, research O.N. required is limiting, and fuels of greater sensitivity can be tolerated as C.R. is increased. The O.N. required increases in orderly fashion, but the increase is smaller as the C.R. increases. R. G. T.

328. Fuels for high compression engines—preliminary study of the selective blending of gasoline distillates from present-day refining processes. W. C. Offutt, J. E. Taylor, and G. B. Swartz, Jr. *Industr. Engng Chem.*, 1949, **41** (10), 2359–65.—The need is stressed for the simultaneous development of fuels and engines so that these can be suitably matched. Any change in fuel anti-knock-quality requirements of automotive engines should be established early enough to allow the refiner to develop methods for economic production of requisite fuels. The mechanical barriers to high C.R. can be controlled by improved design. Thus an upward trend in C.R. will follow the economic production of fuels of sufficiently high O.N. Test data must be obtained on the newly designed engines. The data here presented summarize the road anti-knock performance of several selectively blended gasolines in special engines of 8 : 1, 10 : 1, 12·5 : 1 C.R. A complete hydrocarbon analysis is shown for the fuels described, since hydrocarbon-type composition is known to affect road performance. R. G. T.

329. Combustion of droplets in a fuel spray. G. A. E. Godsave. *Nature*, 1949, **164**, 708.—The burning rate of commercial fuels and pure hydrocarbons has been measured by cinematographic examination of single droplets (200–1000 μ dia) burning in still air on a silica filament. It was found that : (1) burning drops evaporate at a rate proportionate to their radii ; (2) the v.p. does not have a predominant effect in determining the rate of burning ; (3) the rate of evaporation depends upon the rate of flow of heat to the droplet and on the specific and latent heat of evaporation of the liquid. All these results have been predicted by mathematical analysis. Theoretical arguments have led to a derivation of the burning rate in terms of the geometric and physical properties of the system, with good agreement between experimental and theoretical figures. Predictions can also be made concerning the effect of fuel characteristics on the burning rate. H. C. E.

330. The effect of natural gasoline on motor gasoline quality. G. R. McPherson and F. Sipos. *Oil Gas J.*, 3.11.49, **48** (26), 72.—Gasoline of balanced volatility may be produced by use of natural gasoline, variation in vapour pressure of natural gasoline, depth of cut taken on straight run, reformed and cracked gasolines may be varied, or amount and degree of reprocessing, such as severity of reforming, may be changed.

The effect of added natural gasoline upon volatility is discussed and results shown in seven figures.

Low-sulphur natural gasolines usually improve lead susceptibility of motor fuels ; and most natural gasolines are of intermediate O.N. G. A. C.

331. Preliminary study of oxidation reactions preceding true combustion in engines. O. Widmaier. *Rev. Inst. franç. Pétrole*, 1949, **4**, 543–54.—Tests were carried out to

determine the effect of induction temp (130–170° C) and C.R. on formation of aldehydes and peroxides in an I.G. single-cylinder test motor with ignition disconnected and driven externally. C.R. was set just below the self-ignition point, mixture richness (0·77–1·1) was varied by altering fuel feed, air (dried) being kept constant. Two groups of gasolines were examined, paraffinic (O.N. 42–89) and aromatic or *iso*paraffinic (O.N. >100). Exhaust-gas analyses were made after steady conditions had been established, peroxides being determined with ferrous thiocyanate, and aldehydes with $NH_2OH{\cdot}HCl$; organic acids could be detected only in traces, but appreciable amounts of CO_2 were formed. Results are given as curves showing quantity of oxidn product against $^1/R$ (where R is mixture richness) for various induction temp. Higher O.N. fuels gave (at equal C.R.) least oxidn products, quantity of these latter is also reduced by addition of T.E.L. When using synthetic (O.N. 42–50) and T.E.L.-containing fuels, considerable amounts of gum (containing up to 3% organically-combined Fe) were recovered from a condenser placed in the exhaust system. Addition of T.E.L. reduces sensitivity of fuel to induction temp and to mixture dilution. V. B.

332. Oxidation, ignition, and detonation of fuel vapours and gases. VIII. Causes of the antiknock property of rich mixtures. R. O. King, W. A. Wallace, and E. J. Durand. *Canad. J. Res.*, 1949, **27F** (4), 211–24.—By using two fuels—*n*-pentane and a commercial fuel containing high B.P. constituents—and by varying the rate of heat addition to the mixtures in air, conditions could be obtained in which nearly all the fuel could be admitted to the engine as vapour, or nearly all as liq. It is concluded that enrichment of the fuel–air mixture used in an engine leads to an anti-knock effect in addition to that due to increased cooling because of the consequent increase in the rate of oxidn of the end gas.

It is also shown that the anti-knock effect of enriching the fuel–air mixture is greatly enhanced when iron carbonyl is added to the fuel. D. F. J.

333. Oxidation, ignition, and detonation of fuel vapours and gases. IX. Cause of the reversal of the antiknock property of rich hydrocarbon–air mixtures. R. O. King, W. A. Wallace, and E. J. Durand. *Canad. J. Res.*, 1949, **27F** (8), 307–10.—Experiments in an unsupercharged engine show that a reversal of the anti-knock effect of enriching a hydrocarbon–air mixture can be obtained. This reversal occurs after mixture strength has been increased beyond that for maximum power. In supercharged aero-engines however, the reversal may occur before mixture strength is increased to the value required for the development of max power. The experimental results, considered in the light of the nuclea theory of detonation, indicate that the reversal occurs when the rate of formation of finely divided carbon by pyrolysis of the fuel provides a pro-knock effect greater than can be offset by the anti-knock effect of the products of the high-temp heterogeneous oxidn reaction. D. F. J.

Lubricants.

334. Properties of soluble cutting oils. Anon. *Mech. World*, 9.12.49, **126** (3292), 685.—Cutting fluids have an important effect on the efficiency of machining operations, and the Production Engineering Research Association of Great Britain (P.E.R.A.) is investigating the properties of cutting fluids and the effect they have on the efficiency of turning, drilling, milling, and other machining operations. Test results will also provide cutting-fluid manufacturers with data on which improvements of their products can be based. Eventually it should be possible to determine to what extent the efficiency of a cutting oil depends on its physical properties, such as analysis, coeff of friction, and visc. The paper discussed briefly a number of the characteristics of cutting oils such as corrosive effect, lubrication quality, the size and distribution of oil particles in suspension in an emulsion of oil and water, the wetting or spreading property of a soluble oil, the rate of dilution of emulsions. A. S.

335. Functional tests for lubricants and their interpretation. T. G. Roehner and E. S. Carmichael. *Lubr. Engng*, Feb. 1949, **5**, 15.—The limitations of conventional physical and chemical tests for lubricants are discussed, and the trend towards functional tests is remarked. A description is given of an hydraulic-pump-test assembly used in the evaluation of hydraulic oils, particularly for machine tools, in which vane wear is used

to assess metal loss, and the pump parts and entire system are inspected for evidence of corrosion and the presence of deposits.

From the data so obtained it is suggested that successful functional testing should be based on the following considerations: availability of accurate data regarding conditions encountered in actual service; extent to which certain field operations can be simulated on a laboratory scale; instrumentation or equivalent means for expressing the test data in numerical terms, so that the ratings of the products need not rely on adjectives difficult to define; reproducibility and repeatability obtainable within significant limits without too much dependence on human equations, and ability to interpret and correlate the data with field experience. J. G. H.

336. Significance of tests and specifications for greases. G. Kaufman. *Lubr. Engng*, Apr. 1949, **5**, 83.—The procedures in common use for the testing of lub. greases, their significance and practical value in specifications are discussed. Tests described include consistency, pressure viscosity, dropping point, oxidation stability, separation tests, evaporation, water susceptibility, and chemical analysis.

It is emphasized that while these tests enable the manufacturer and consumer to check consistency of product the only assurance of a satisfactory lubricant is proved field performance. J. G. H.

337. Laboratory evaluation of E.P. gear oils. L. B. Sargent, I. S. Holarik, and E. M. Kipp. *Lubr. Engng*, Oct. 1949, **5**, 226–30.—In view of the reputed lack of correlation of tests on accepted test equipment, forty-one proprietary gear lubricants, constituting a representative cross-section of commercial heavy-duty extreme-pressure gear lubricants were tested on the Timken, Shell Four-Ball, and Falex machines. Physical properties of the selected lubricants and the results of the tests are presented in tabular form, and it is concluded that a limited correlation exists between Falex and Four-Ball ratings. The lack of correlation with these ratings of results obtained on the Timken machine are attributed to its extreme sensitivity to visc variations within the range represented by the lubricants under test. J. G. H.

338. Antifriction bearing developments. A. S. Murray. *Lubr. Engng*, Dec. 1948, **4**, 252.—Two new methods of lubrication are described, and the specific fields of application for each process are detailed. Oil-mist lubrication, employed in the lubrication of small high-speed bearings, uses a motor compressor unit which forces compressed air into an oil reservoir, where it overcomes the surface tension of the oil and breaks it up into a fine mist in which form it will carry reasonably long distances through connecting lines without separating out and collecting in pockets. The system is applicable where bearings may be lubricated with 20 drops of oil per hr or less and where temp rises must be kept to a minimum, and in high-speed spindle bearings where bearing cleanliness is essential. Necessary conditions for efficient operation include a clean air–oil-mist supply and a correct proportioning of oil and air, this being determined experimentally.

Flood lubrication has been applied to high-speed rolling-element bearings and, by employing oil in sufficient quantities to act as both coolant and lubricant, has facilitated the employment of these bearings at speeds and temp which presented difficulties with other types. The quantity of oil used, of the order of 1–1½ gal per bearing per min, is such that the oil actually lubricating the surface contacts is not allowed to reach carbonizing temperature. J. G. H.

339. Friction of dry and lubricated surfaces as determined by the stick-slip method. J. Morgan, M. Muskat, and D. W. Reed. *Lubr. Engng*, Apr. 1949, **5**, 75.—The wide variations in the friction coeff for metal on metal, dry, and for metal on metal, wet, are remarked, and results are given of a friction survey of various metal combinations as made with stick-slip apparatus built in the Gulf laboratories on the basis of that developed by Bowden and Leben. The apparatus is described, and specific points affecting the accuracy of the data are discussed. Methods of calculation are explained, and the experimental results obtained tabulated. The lubricants employed comprised a straight mineral oil, the same with the addition of 3% oleic acid and a silicone lubricant. It is observed that the stick-slip motion is uniform and regular for soft, low m.p. metals, particularly when dry. Both static and kinetic friction are lower for the

mineral oil than for the silicone, and are least of all for the oil with the additive. Almost without exception for dry surfaces and in most cases with mineral oil and the silicone, static friction is higher than kinetic. J. G. H.

340. Progress in instrument lubrication. H. Gisser. *Lubr. Engng*, Aug. 1949, **5**, 175.—The general requirements of instrument lubricants are enumerated, and the development of special-purpose lubricants is outlined with notes on diesters, silicones, and " Ucon " lubricants. Oxidn stability and its relation to the general technique of instrument lubrication is discussed, and the application of conventional tests to instrument lubricants is described. J. G. H.

341. Properties and uses of a new series of lubricants. Anon. *Scientific Lubrication*, Nov. 1949, **1**, 16–17.—The properties and special applications of silicone greases, DC 33, DC 41, and DC 44, introduced by the Dow Corning Corporation, are described, and mechanical modifications necessitated by their use are outlined. Data are also presented on silicone valve-sealing grease. J. G. H.

342. Emulsions and lubrication—1. A. V. Brancker. *Scientific Lubrication*, Mar. 1949, **1**, 12.—The fundamental principles of emulsification are outlined, and the theories of orientation and wetting discussed, together with the functions of surface-active agents. J. G. H.

343. Evaluation of engine preservative oils—2. H. Sellei. *Scientific Lubrication*, Nov. 1949, **1**, 11–12.—Corrosion inhibitors are grouped on an electrochemical basis in four classes : proton accepters, electron accepters, overvoltage modifiers, and barriers. Adsorption, polar compounds, contact angles, and multilayer protection are discussed, and methods described for the quantitative measurement of rust. J. G. H.

344. Cylinder lubrication of air compressors. Anon. *Scientific Lubrication*, Nov. 1949, **1**, 9–10.—The dangers of overlubrication of air-compressor cylinders are remarked, and the advantages of using low-viscosity oil are set out. Typical lubrication systems and vapour filters are described, and problems of air contamination discussed. J. G. H.

345. Some aspects of diesel cylinder lubrication. E. B. Watson. *Lubr. Engng*, Aug. 1949, **5**, 180.—Correct cyl lubrication should ensure that the rate of wear of cyl, pistons, and piston-rings is within acceptable limits, that the rate of formation of piston deposits is kept at a min and that oil consumption will not exceed acceptable limits. The formation and maintenance under all engine-operating conditions of an oil film between mating services is stressed as the basis of cyl lubrication. The processes incident to cyl wear are enumerated, and the effects of oil visc, volatility, and additive treatment on the rate of wear are discussed. The formation of engine deposits by the deterioration of the lubricant is explained, and the function of heavy-duty oils in combating this formation is described. J. G. H.

346. Lubrication of land and marine oil engines—2. Anon. *Scientific Lubrication*, Mar. 1949, **1**, 14–17.—The significance of oil consumption as a criterion of engine condition is discussed, and factors affecting oil consumption are enumerated with consumption data for individual engines. The effects of cold starting, piston-ring adjustment and design, bearing clearances, and bearing oil grooving, together with the chrome plating of cyl liners are considered. The function of baffle plates in reducing oil splashing is described, and oil losses from gudgeon pins are considered, together with the significance of correct oil pressure. J. G. H.

347. Lubrication of railway rolling stock. *Lubr. Engng*, Aug. 1949, **5**, 168.—A discussion of lubrication practice for railroad cars is followed by a consideration of the special requirements of steam and diesel engines. J. G. H.

348. Reversing lubrication system. Anon. *Scientific Lubrication*, Nov. 1949, **1**, 18–19.—The Trabon system of centralized lubrication for machinery is a reversing, single-line system, requiring relatively low pressures, employing totally enclosed feeders and adapted for manual or mechanical drive. J. G. H.

349. Planning a steel mill lubrication program. W. M. Schuck. *Lubr. Engng*, Feb. 1949, **5**, 10–14.—Special problems involved in formulating a steel-mill lubrication programme include the care of machines of varying ages, calling for an exceptionally wide range of lubricants. It is emphasized that lubrication is a maintenance problem, and as such should be either under direct maintenance control or closely tied in with maintenance personnel.

A lubrication programme is put forward comprising training, plant-lubrication survey, periodic testing of major closed oil-circulating systems, consumption control report, simplification within division departments, testing of new products, engineering investigation of new equipment, lubrication practices, and codification of lubricants. The significance of each of these components is indicated, and it is stressed that codification is a refinement only to be tackled when the rest of the programme is well under way. J. G. H.

350. Lubrication of textile equipment. J. R. Crotty. *Lubr. Engng*, Apr. 1949, **5**, 71–4.—The wide variation in textile-loom lubricants as indicated by specifications submitted by oil companies is discussed, and the results of comprehensive tests on a wide range of products suggest that for oils, chemical analysis, flash, fire, and viscosity are of little significance. The value of highly refined as compared with straight mineral oils of equivalent viscosity is remarked, and compounded oils, with oils of the dripless variety, although affording superior performance, are condemned on account of separation and blocking of the filters. Specifications are presented for oils for breaking in looms and for normal operation, together with greases for plain and anti-friction bearings and for starting looms. The dangers of overlubricating are emphasized and a specimen lubrication schedule for loom components is included.

The value of recently developed additives for special purposes is stressed, and the increasing tendency to base purchasing specifications on performance standards is noted with approval. J. G. H.

Bitumen, Asphalt, and Tar.

351. Aggregate retention on bituminous seal coats. R. J. Hank and Marshall Brown. *Rds and Streets*, Nov. 1949, **92** (11), 72.—The influence of various factors upon the aggregate retention on bituminous-seal coats has been investigated.

1. The source of the bitumen does not have any pronounced effect upon aggregate originally embedded and retained. There is, of course, some difference in aggregate-retaining properties between bitumens of different sources due to differing penetration indices.

2. Decrease in penetration of the bitumen causes a gradual increase in aggregate loss.

3. Adequate rolling is essential for asphalt cements, but not so critical for cutback bitumens.

4. Cutbacks and bitumen emulsions are both superior to asphaltic cement, rapid curing being essential in the case of cutbacks.

5. Aggregate grading can have a big effect. A high " fines " content hinders aggregate retention, although this is less noticeable with precoating or emulsion work.

R. H.

Special Hydrocarbon Products.

352. Cutting oils and coolants. H. M. Harman. *Scientific Lubrication*, Mar. 1949, **1**, 3–6.—The functions of cutting oils and coolants in machine-tool operation are outlined, and the situation of the actual point of application is discussed with details of distribution systems. The composition of cutting oils is considered, and the special requirements for grinding coolants are enumerated, together with data on equipment for the removal of contaminants from grinding coolants. J. G. H.

353. Effects of cutting fluids and power requirements in metal cutting operations. A. O. Schmidt and G. V. B. Sirotkin. *Lubr. Engng*, Dec. 1948, **4**, 261–5.—The function of cutting fluids in improving cutter life at high cutting speeds is discussed. The use of the drill calorimeter in determining the cooling qualities of a cutting fluid is described with illustrations from drilling and milling operations, and it is noted that no appreciable reduction of power occurs with the application of cutting fluids so long as rubbing

friction on non-cutting surfaces is absent. Results of testing a series of cutting fluids revealed that water is the most effective portion of any coolant when milling at high surface speeds. J. G. H.

354. Non-flammable hydraulic fluids. C. M. Murphy and W. A. Zisman. *Lubr. Engng*, Oct. 1949, **5**, 231–5.—The functions, properties, and methods of testing hydraulic fluids are outlined, and typical requirements of U.S. Government specifications are presented in tabular form. Detailed procedures for flammability tests are described, and it is concluded that no available petroleum-base or castor-oil-base hydraulic fluid is sufficiently flame-resistant. Tests are described on esters of carboxylic acids and on organic phosphates, neither of which proved entirely satisfactory. A tabular comparison is presented of the properties of some of the more promising aircraft hydraulic fluids. J. G. H.

355. Insulating oil. Its care and treatment in small establishments. J. W. McQuillen. *Electr. Times*, 1949, **116**, 827–30.—Removal of C and H_2O from switch oils is briefly discussed. Economics of recovery are considered in terms of oil and filter cost, their useful life and interest rates. Quantities of oil <100 gal are not worth recovering. For small amounts a centrifuge is the cheapest purifier. The use of filters packed with powders rather than with paper is preferred. Several proprietary filters and centrifuges are illustrated. V. B.

356. Pulmonary hazard of the ingestion of mineral oil in the apparently healthy adult. L. Schneider. *New Engl. J. Med.*, 1949, **240**, 284–91.—Habitual ingestion of mineral oil by mouth gives rise to risk of pulmonary complications. The pathology of chronic mineral-oil-pneumonitis is described and the literature briefly reviewed (eighteen references). Particular attention is given to diagnosis by X-ray photography. Confirmatory tests are detection of mineral oil in the sputum and in matter obtained from the affected lung by aspiration biopsy. Five case reports (males over sixty) are given, with X-ray photographs; the dosage in these cases was in the range of 15–50 ml daily for periods of three to twenty-five years. V. B.

Derived Chemical Products.

357. Synthetic detergents. J. W. McCutcheon. *Soap Sanitary Chem.*, Aug. 1949, **25** (8), 33, and following issues, pp. 42 and 41.—The chemical and physical properties and types of surface-active compounds are briefly outlined, and the development, manufacture, uses, and world market outlook are briefly reviewed. A list, giving the trade names, manufacturer, class and formula, main uses, form, per cent concentration, type, and data relative to further uses, is given of more than 750 synthetic detergents. W. H. C.

358. Synthetics in water systems. Anon. *Soap Sanitary Chem.*, Oct. 1949, **25** (10), 77.—Brief summaries are given of two papers read at the national meeting of the American Water Works Association held in Chicago, on the effect of synthetic detergents in municipal water.

W. U. Gallaher attributed the difficulties met with in the coagulation of water during the lime-softening process to the detergent content of the water. He found that only a small amount of detergent interferes with the coagulation and settling of the water, especially if the water contains a small amount of organic matter.

J. T. Cross described a wider range of tests covering six detergents at different concn, and particularly at concn of 5 p.p.m. Results are given of the effect of various coagulants in samples containing the above concentration of detergent.

Alum gave poor coagulation with five of the detergents, addition of lime to the alum increased the pH, and decreased interference with coagulation, ferric sulphate gave results similar to alum. Without lime two of the detergents showed pronounced interference with coagulation. All detergents gave poor settling with chlorinated copperas as coagulant; interference was only moderate upon addition of lime. W. H. C.

359. The use of polarized infra-red radiation in the study of doubly oriented long-chain polymers. E. J. Ambrose, A. Elliott, and R. B. Temple. *Proc. Roy. Soc.*, **A**, **1949**, **199** (1057), 183–98.—An investigation has been made into the structure and orientation

of high polymers by means of polarized infra-red radiation. The work has shown that infra-red spectroscopy can furnish evidence for double orientation in rolled sheets of nylon 66, polyvinyl alcohol, and (with less certainty) polythene. Double orientation could not be detected in polyvinyl formate, acetate, chloride, and polyvinylidine chloride.

It is shown that in nylon the N–H bond is bent by hydrogen bonding forces, the angle between this bond and the plane of the skeleton being thereby reduced from 39° (the valency angle) to 22°.

The absence of dichroism in the O–H frequency in the spectrum of polyvinyl alcohol when a doubly oriented sample is examined strongly supports the structure of polyvinyl alcohol recently proposed by Bunn. W. H. C.

Miscellaneous Products.

360. Chlorinated rubber in the Paint Industry. B. S. Gidvani. *Paint Mnfr*, Dec. 1949, **19**, 410.—The chlorination of rubber is usually carried out in solution, and catalysts such as iodine may be used to accelerate the rate of chlorine absorption. The product is believed to be a mixture of two materials. Recent work indicates that the course of the reaction is substitution, then substitution and addition simultaneously, followed by 95% substitution. Some details of the manufacture are considered.

The properties of chlorinated rubber depend upon the degree of chlorination. In the commercial product the chlorine content is between 60·5 and 68·8%. Chlorinated rubber is non-inflammable and has outstanding abrasion and shock-resisting properties. It gives hard, brittle, and non-resilient clear-films which are very resistant to chemical attack. The action of solvents for chlorinated rubber is considered, benzol, toluol, and xylol are all excellent. Chlorinated rubber is extremely inert, but ultra-violet rays and heat decompose it appreciably.

The optimum properties of the film are developed only when the ratio of plasticizer to chlorinated rubber is carefully selected. The porosity of the film may be tested by dipping coated iron rods into 2% $CuSO_4$ solution acidified with a trace of H_2SO_4. Discontinuity of the film is revealed by deposition of copper at the sites of pores. Most commonly used pigments are suitable with chlorinated rubber, but ultramarine and prussian blues tend to gel the paint; bronze and aluminium powders are also unsatisfactory. The pigment has to be ground in the plasticizer and/or resin solution, and the pigmented paste dispersed in the rubber solution. Incorporation of a small quantity of wetting agent, such as zinc naphthenate, in the pigment paste is found helpful.

Chlorinated-rubber paints find application in workshops, factories, chemical works, pulp and paper mills, gasworks, swimming-pools, etc. D. K.

361. Physical structure of paint films—rigidity. Anon. *J. Oil Col. Chem. Assoc.*, 1949, **32**, 499.—Mechanical properties of films of protective coatings have an important bearing on their durability. Many films fail by cracking, *i.e.*, magnitude of stress in film exceeds cohesive forces of film structure. These stresses may be due to: (*a*) dimensional changes of film and substrate due to temperature or humidity changes or (*b*) by dimensional changes in film itself, due to chemical changes occurring during weathering. The relationship between mechanical properties and type of polymer molecule in polymeric materials is discussed. Fresh paint is relatively soft and elastic, whereas on weathering it hardens and becomes less elastic; it is suggested that the freshly dried film is a polymeric material with few cross-links, but under weathering conditions cross-linking progressively develops till it assumes the mechanical properties of a heavily cross-linked polymer.

A method of determining the dynamic rigidity of films is described. Tabulated results for the dynamic rigidity of films of a tung-oil–modified-phenolic-resin varnish pigmented with TiO_2 are presented. These results show that dynamic rigidity is dependent on film thickness, and that there is a change of rigidity on outdoor exposure.

Investigations made give some confirmation of the thesis that "dry" films of protective materials are frequently non-homogeneous, due to growth of rigid material from the surface downwards. Durability is affected by film thickness. D. K.

362. Blistering of paint films on metal under sub-marine conditions. P. J. Gay. *J. Oil Col. Chem. Assoc.*, 1949, **32**, 488.—The mechanism of liq blister formation on prolonged immersion of paint coatings applied to metal was investigated. Experi-

ments showed that oil-paint films can absorb water ranging from 20 to 350% by volume depending upon composition and age of the film. Diffusion is inadequate to explain the building up of the pressure required for blister formation, osmotic or endosmotic flow seem to be the mechanisms which occur. Osmosis does not explain all the phenomena, electrical differences in the film, at the interface and on the metal surface, play a part. From observations made on painted steel it appears that corrosion of the steel surface accompanies blister formation.

Experimental work is discussed under the following headings: (*a*) Composition of fluid in blisters in paint films on steel; (*b*) behaviour of paint and varnish films on corrodible and non-corrodible surface during immersion in liquids of various osmotic activities; (*c*) interrelation between corrosion of painted steel and blistering of films. The study involved observations on: (i) painted steel panels immersed in the sea; (ii) similar panels subjected to accelerated corrosion tests in the laboratory; (iii) painted steel and glass rods subject to controlled immersion tests in dist water and saline solutions.

Results indicate that blistering on steel is a two-stage process with the paint or varnish film acting first as an absorptive gel and later as a semi-permeable membrane and that there is a definite chemical and electro-chemical connexion between blisters and corrosion occurring nearby.

The weakening of adhesion between paint and metal, the first stage in blister formation, is attributed to the alkali produced under the film as a by-product of the corrosion process. D. K.

363. The mechanism of the protective action of an unpigmented film of polystyrene. J. E. O. Mayne. *J. Oil Col. Chem. Assoc.*, 1949, **32**, 481.—It is believed that a film of polystyrene decreases the rate of corrosion by preventing either water, oxygen, or chloride ions from reaching the metal surface. Results of tests show that the weight of water which could diffuse through unit area of polystyrene film in a year is ten times greater than that consumed by an unpainted specimen immersed in seawater. Thus the protective action cannot be attributed to exclusion of water from the metal surface. The weight of oxygen which could diffuse through unit area of a polystyrene film immersed in seawater for a year has been calc. The result is of the same order as that of oxygen consumed by an unpainted specimen.

The diffusion of chloride ions through polystyrene films was studied, and the apparatus used is described. Results indicate that positively charged ions pass through the film more easily than negatively charged ions, and that the thicker films are almost impermeable to chloride ions; moreover, the difference in permeability of the ions suggests that the film acquires a negative charge when immersed in KCl solution. Further work indicates that the application of a potential causes chloride ions to migrate through a polystyrene film faster than they move under a concn gradient alone, calculations show chloride ions pass through the film only with difficulty, and the major part of the current is carried by other ions.

It is concluded that a polystyrene film interposes a high ionic resistance between the anodic and cathodic areas on the surface of the iron, and the corrosion current is thereby reduced to a small value. The resistance of the film is slowly broken down, first by taking up water and later by inward migration of ions; thus corrosion progressively increases. It is thought probable that films of mineral oil, asphalt, and bitumen function in a similar manner. D. K.

364. Gelling of self-polishing emulsion waxes. A. H. Kroner. *Soap Sanitary Chem.*, Oct. 1949, **25** (9), 137.—The gelation of aqueous colloidal emulsions of waxes can be caused by a number of different factors, such as hydrolysis, oxidation, polymerization, decomposition, catalytic reaction, or microbial action. As gelling is a gradual transition from sol to gel and may take a long time to develop, a rapid method of testing is required for its evaluation. The N.A.I.D.M. test method for the purpose is described. Its function is to accelerate the gelling of the sample by an oven test at 125° F. A minimum testing period is two weeks, which corresponds to a standing time of six months.

The formulation of a satisfactory product is described. The basic ingredients are carnauba, candellia and paraffin waxes, casein, shellac, and water. As emulsifiers, compounds containing an amide group are used. The choice of these usually depends

on their capacity for making the wax film more or less water-resistant. Soap, oleic acid, and borax are also ingredients. The ingredients and their amounts are given and discussed as to their functions and effects on manufacture and stability of the product. The procedure is by peptization, the purpose of which is to obtain a glossy film on drying. Usually these polishes are slightly alkaline with a pH number of from seven to nine. Heat, oxygen, etc., and even the container itself may affect the product after a time. W. H. C.

365. White mineral oil, a selective plasticizer. R. K. Rhodes. *Mod. Plastics*, Nov. 1949, **27** (3), 142.—White mineral oil for use as plasticizer must be of United States Pharmocopæia grade. It must be free from unsaturated fractions, as measured by its colour change when treated with 95% H_2SO_4, its distillation range must fall between 600° and 760° F, and it must have flash and fire points above 350° and 400° F respectively. This grade of white oil has a Saybolt colour of 30+. A table is contained in the article giving the amounts of white oil which should be used in conjunction with different resins. O. M.

366. Surface film studies on DDT-oil larvicides. B. F. Burgess. *Soap Sanitary Chem.*, Aug. 1949, **25** (8), 127.—The results of earlier work are shown in which the I.B.P., sp. gr., visc, spreading pressure, and type of film produced of 0·5% surface-active agent, Triton B.1956 and 1% DDT in sixteen named commercial oils or solvents. Of these only four gave continuous films when applied at the rate of 1 gal/acre.

The results of spreading-pressure tests and film types are shown for solutions containing 0·5% of fourteen named surface-active agents and 1% DDT in kerosine. Only six gave continuous films, the four having the highest spreading pressure were : Ethofat 142/2C, Triton N.1956, Nonisol 219, and Solvadine EO.

Further tests of combinations of the four best solvents, *i.e.*, kerosine, Sovacide Pd544C (Soc.-Vac. Co), medium aromatic oil 8277 (Shell Oil Co), and 70 pale oil (Texaco Co.), and the four best surface-active agents noted above, showed that all four gave the highest spreading pressures, and a continuous film, with the kerosine.

Toxicity tests on *Anopheles* mosquito larvæ are described, in which each of the four surface-active compounds at 0·5% concn, and 1·0% DDT in kerosine were used at the rate of 1 gal/acre. The results showed that Ethofat 142/20 excelled the others. It produced a continuous, uniform, and stable film and had the highest spreading pressure, and, at the rate indicated, effected a 50% knockdown in 15 min and a 100% kill in 100 min. The film produced effectively penetrated biological films on streams and remained stable for 72 hr. W. H. C.

Engines and Automotive Equipment.

367. E-H hydraulic Servo injection pump. Anon. *Gas Oil Pwr*, 1949, **44**, 266–9.—Perfect combustion in a C.I. engine can be achieved by atomizing the fuel as completely as possible, and by delivering it to the cylinder as quickly as possible. To accomplish these ideals the injection pressure must be very great (10,000–20,000 p.s.i.), and the mechanism described below does this by actuating the fuel-pump by fluid pressure from a hydraulic generator, which operates as follows.

A cam-operated plunger working in a ported sleeve is so arranged that on rising it closes all ports and compresses lub. oil in an accumulator to a pressure of about 3000 p.s.i. When travelling at its maximum velocity the plunger uncovers a port communicating with the injection pump, thus creating a sonic wave travelling through the oil medium at 4700 ft/sec, and under normal conditions occupies the time taken for about 4° of crankshaft movement. The first movement of the fuel-pump plunger is therefore very rapid, and this is followed up at a reduced pressure as the oil is displaced. Due to the force on the fuel-pump plunger being a wave, the actual pressure is much greater than that of the oil in the accumulator, and may attain 19,000 ft/sec. Since the wave front is very steep, the rise and fall of pressure is very abrupt. This initial pressure is followed by a sustained pressure due to plunger displacement, which may be extended over the required number of crankshaft degrees. H. C. E.

368. A new high-performance engine indicator of the strain-gauge type. C. S. Draper and Y. T. Li. *J. Aero. Sci.*, 1949, **16** (10), 593.—Pressure changes in the working fluid

largely determine the performance of heat engines. For this reason, accurate pressure indications are of primary importance for studies of engine operation. Pressure indicators have been in use for many years, but performance defects have restricted their value even for laboratory and test-stand work. The operating limitations have been due to the fact that available pressure receivers have been sensitive not only to pressure, but also to temp, to mechanical strains due to mounting effects, and to mechanical vibrations in the walls of the pressure chamber. It is the purpose of this paper to describe the features of a new pressure receiver using a high-flexibility catenary-type diaphragm and a temp-compensating wire-wound strain gauge to give satisfactory pressure-measuring characteristics with greatly reduced response to temp and extraneous mechanical effects. I. G. B.

369. High-speed marine engines at Earl's Court. Anon. *Gas Oil Pwr*, 1949, **44**, 272–6.—The following manufacturers exhibited engines which are either entirely new, newly converted to marine service, or old engines in improved form :—

(A) Associated Manufacturers Co. (London) Ltd.
(B) Arthur Bray.
(C) British Marine Distributing Co. Ltd.
(D) W. H. Dunn & Co. Ltd.
(E) Methway Marine Ltd.
(F) Henry Meadows Ltd.
(G) General Motors Ltd.
(H) F. Perkins Ltd.
(J) Turner Manufacturing Co. Ltd.
(K) University Marine Ltd.

Brief specifications of the engines exhibited are given in the following table :—

Maker.	Engine.	Cylinders.			Max. b.h.p.	Max. r.p.m.	Fuel consumption.	Stroke.
		No.	Bore.	Stroke.				
A	Four 260	4	3½ in	5½ in	55	1800	—	4
A	Six 572	6	4¼ in	5½ in	150	2200	0·425 lb/b.h.p/hr	4
B	6-BDMR-230	6	3 7/16 in	4½ in	60	2400	—	4
C	MFD-6	6	85 mm	120 mm	120	2000	0·4 lb/b.h.p/hr	2
D	4DSM	4	90 mm	120 mm	20	1000	—	4
E	MD100	6	4½ in	5½ in	100	1550	0·36 pt	4
E	MD120	6	5 in	5½ in	120	1550	—	4
F	970	6	5·9 in	5·9 in	180 •	1650 •	—	4
G	GM71	6	4¼ in	5 in	140 •	1800 •	—	2
H	S6M	6	4¼ in	5 in	100	2000	—	4
J	IV95	1	3½ in	4½ in	8	1500	—	4
J	4V95	4	3½ in	4½ in	34	1500	—	4
K	—	2	85 mm	100 mm	15	1800	0·42 pt	4

• Continuous rating. A. S.

370. Tests of standard Doxford engine using heavy fuel. Anon. *Motor Ship*, Dec. 1949, **30** (359), 336.—The paper contains the builder's report of trials made on a 3300-b.h.p. Doxford engine on heavy fuel. The fuel used was "Ordoil" supplied by the Anglo-Saxon Petroleum Company. The experience gained during these tests indicates that the standard Doxford engine will operate satisfactorily on "Ordoil" or similar fuel of viscosity up to 1500 sec Redwood No. 1. at 100° F. A. S.

371. Excessive cylinder liner wear. E. Th. Christiansson. *Motor Ship*, Dec. 1949, **30** (359), 361.—Increased wear of cylinder-liners in motor ships during past four or five years is a serious problem. In many cases the average wear of cylinder-liners of main engines per 1000 running hours has trebled in recent years. In addition to this problem is that of the increased number of fractured pistons and cylinder-heads. Apart from the heavy costs resulting from these troubles, there is also the question of higher lub.-oil consumption for trunk-piston engines due to heavier wear of cylinder-liners. An increase of lubricant consumption by 50–100% is by no means rare. The

paper considers a number of factors which in the past have been considered responsible for the wear in cylinder bores. As a result of recent experience, it is suggested that two independent but co-acting causes have a strong influence on wear, viz : (1) electric currents produced in the ship and engine ; (2) alterations in composition of diesel oil. These two points are then discussed further. A. S.

372. Diesel manufacture. Anon. *Auto. Engr*, Nov. 1949, **39** (521), 477.—The paper contains a survey of the methods employed by Dennis Bros. Ltd. for production of cylinder-blocks, camshafts, crankshafts, connecting-rods, etc. A. S.

373. Crankcase explosions. Anon. *Engineer*, 1949, **188**, 556–7.—The following were the main points and opinions raised in a recent discussion on this subject between various speakers of the Diesel Engine Users Association and the Institute of Marine Engineers : (*a*) crank-chamber explosions have occurred on steam-engines of the enclosed, pressure-lubricated type as well as on I.C. engines ; (*b*) a vulnerable point as regards overheating and ignition of crankcase vapours is the piston-pin, leading to piston seizures ; (*c*) trouble has been experienced in I.C. engines of the crosshead type due to expansion of the crosshead in the guide ; (*d*) there should be an inscription on all oil-engines to the effect that should any accessible part appear to be overheated the engine should be allowed to cool down before any casing door is opened ; (*e*) oil-coolers in general are too small ; (*f*) engines should not be allowed to run overloaded ; (*g*) more elaborate instrumentation to gauge condition of inaccessible parts is desirable ; (*h*) ignition due to piston seizure is less likely with aluminium-alloy pistons than with cast-iron pistons, because of the lower melting point of aluminium (1200° F as against 2200° F) ; (*i*) piston gaps should not be less than 0·003 in per in dia ; (*j*) personnel should be employed who really understand what they are watching ; (*k*) with modern high-speed engines the density of the mixture of oil droplets and vapour in the crankcase is such that it is too rich to be explosive ; (*l*) crankcase explosions can be avoided by ventilating the crankcase to a maximum degree, which means oil-coolers and bigger fans. A. C.

374. Knock-free diesel operation. Anon. *Auto. Ind.*, 15.5.49, **100** (10), 37.—London Passenger Transport Board, operating more than 5000 diesel buses, is stated to have eliminated diesel knock by the use of pilot injection with a resultant degree of silence comparable to that of a gasoline engine, coupled with improved performance. The system, developed by the Atlas Diesel Co. of Stockholm, employs a first or pilot injection followed by the main charge, this being obtained by a combined pump and injector with two spill ports in the pump sleeve so arranged in size and shape that pilot injection is effected with the use of a two-stage cam contour. Pilot injection is constant at all deliveries, being the amount of fuel necessary for idling. J. G. H.

375. Gas turbine fuel systems. W. A. Andrews. *Flight*, 20.9.49, **56** (2130), 512.—A survey is given of the primary factors in control-system design. I. G. B.

376. Combustion chambers for open-cycle marine gas turbines. R. F. Darling. *Motor Ship*, Dec. 1949, **30** (359), 358.—The paper describes a number of the combustion problems encountered in the gas turbine and their influence on the design of combustion chambers for gas turbines of the open-cycle type. It then goes on to discuss design features connected with combustion chambers for marine gas turbines and the experience gained as a result of tests on this type of prime mover. A. S.

377. Fuel spray nozzles for aircraft gas turbines—1. J. A. Bolt and M. F. Saxton. *Auto. Ind.*, 15.5.49, **100** (10), 30.—The functions of fuel-spray nozzles in aircraft gas turbines are described, and their place in the combustor assembly as a whole is discussed. Requirements for the ideal fuel nozzle are enumerated, and the characteristics of the types of nozzle at present employed are outlined. J. G. H.

378. Fuel spray nozzles for aircraft gas turbines—2. J. A. Bolt and M. F. Saxton. *Auto. Ind.*, 1.6.49, **100** (11), 36.—The operation of the variable-orifice nozzle is described, and steam and compressed air are compared as atomizing agents. Difficulties experienced when spray nozzles are used as fuel meters are outlined, and the employment

in this connexion of fuel dividers is discussed. The extensive use of the duplex type of nozzle is noted, and the importance of the ability of the nozzle to handle dirty fuel is emphasized. J. G. H.

379. Gas turbines for power generation in warships. Anon. *Mech. World*, 25.11.49, **126** (3280), 613.—The Admiralty are considering possibility of developing a gas-turbo-generator suitable for H.M. ships. Advantages of gas turbine are low maintenance, compactness and light weight, quick starting, etc. Fuel consumption of gas turbines in their present stage of development is high compared with the diesel, although comparable with ships' steam turbo-generators. Practical experience is necessary to determine the extent to which high fuel consumption is outweighed by the advantages mentioned above. The Admiralty have placed a contract with W. H. Allen, Sons & Company, Ltd., for a 1000-kW gas turbine and generator for base-load operation. This set consists of an axial compressor of 4/1 pressure ratio, delivery to an annular-type heat exchanger, a compressor-turbine, and a free-power turbine. The generator is driven through an epicyclic reduction gear. The article contains an illustration showing the arrangement of the complete unit, and also gives performance details. The set has been designed for operating in both temperate and tropical conditions. A. S.

380. Anglo-French opposed piston engine. Anon. *Gas Oil Pwr*, 1949, **44**, 257.—These engines are constructed in two sizes; one with two cylinders (four pistons), and the other with four cylinders (eight pistons). The cylinder size is 88 mm bore and 102 mm stroke per piston, giving for the two-cylinder unit a swept volume of 2·5 litres. The max outputs are 60 and 120 b.h.p. respectively at 2000 r.p.m. The compression ratio is 16 : 1, and the max b.m.p.s are 81 p.s.i. at 1500 r.p.m. and 86 p.s.i. at 1600 r.p.m. respectively. Specific fuel consumption at full speed and load is *ca* 0·4 lb/b.h.p.hr.

The cylinders are disposed horizontally at right angles to and directly above the crankshaft. The pistons carry three pressure and two scraper rings. The outer end of each piston is connected *via* a rocker beam to the small end of a connecting-rod. Forced-feed lubrication is supplied to all bearings and to the pistons, which are cooled thereby.

Four figures illustrate the constructional details of the engines. H. C. E.

381. Piston assemblies. J. L. Hepworth. *Auto. Engr.*, Dec. 1949, **39** (522), 528.—The paper reviews a number of different types of piston failures in road-transport oil-engines. The review covers piston breakages, seizures, ring sticking, land breakage, land scuffing, groove destruction. Also discussed are the various limiting factors of piston life as indicated by the oil consumption of the engine. Dangers of overscraping new engines are emphasized, and a method of retaining a minimum consumption over a long life is suggested. Examination of the rates of wear of the different components of the piston assembly reveals the fact that the weakest point is the compression ring. Results obtained in service tests with different piston-ring materials are given, and improved materials are suggested. The results indicate that chromium-plated piston-rings give the best results, and these are recommended for use as the upper compression ring. Suggestions are finally given for designing the successful oil-engine piston. A. S.

382. World's airline figures 1949. Anon. *Aeroplane*, 25.11.49, **77** (2007), 729.—This is a table of the world's airline statistics for the year 1948 which were collected from the airline companies. Details include names of operating companies, number and type of aircraft fleet, staff, total route mileage, passengers, mail, and freight weights. I. G. B.

383. Canberra. Anon. *Flight*, 15.12.49, **56** (2138), 765.—A design analysis of Britain's first jet bomber is given, together with the usual structural cutaway drawing, and sketches and photographs of detailed points in the assembly. I. G. B.

384. Proteus and coupled Proteus. Anon. *Aeroplane*, 9.12.49, **77** (2009), 783.—This account of the Proteus outlines the technical characteristics of both single and

double form of the design, and the photographs of progress follow the technical description of the coupled gear-box published in *Aeroplane*, 6.8.48. I. G. B.

MISCELLANEOUS.

385. Fuels—their present and future utilization. W. M. Holaday, T. E. Albright, R. L. Apjohn, and L. R. Steffens. *Oil Gas J.*, 10.11.49, **48** (27), 277.—The authors point out that less than one-third of energy consumed in the U.S.A. is used effectively, and propose changes in utilization of fuel, considering reserves and efficiency of utilization.

Principal sources of energy are coal, petroleum, and natural gas, the latter two accounting for about 50%. Transport requirements amount to 36% of net energy requirements, and should be subject to greatest reduction by improved utilization efficiency. Automotive efficiency can be improved by raising C.R. in engines, by supercharging, and by use of automatic transmissions.

If a petroleum shortage occurred in the future, use of petroleum must be diverted from fields where alternative fuels could give similar performance; with simultaneous improvement in utilization efficiency in all applications. Eight figures and three tables illustrate the article. G. A. C.

386. Canadian refining. G. Weber. *Oil Gas J.*, 17.11.49, **48** (28), 66.—A review of the Canadian petroleum industry is given. The 1949 consumption of petroleum fuels was expected to reach 95 million brl, an increase of 45% over the 1946 figure.

On completion of projects, rated capacity will be 347,800 brl daily.

Quebec has replaced Ontario as principal refining province, and new construction will make Montreal a refining centre of world importance. Ontaria refineries mostly process Illinois' and Mid-Continent crudes.

Tables show Canadian refining capacity, crude receipts by refineries, and shipments to Canadian refineries from other countries. G. A. C.

387. The human factors in the design of manual machine controls. L. E. Davis. *Mech. World*, 16.12.49, **126** (3283), 695.—A great deal of attention has been devoted to investigating methods of work and to formulating general principles governing the development of effective working methods. An important factor influencing methods of work is the design of tools, equipment, and machinery provided for the job. At the same time human factors must also be carefully considered when designing equipment. The purpose of this report is to determine the factors making for optimum control and speed usage of handwheels, cranks, and cross-bars under conditions of application involving single settings of indicators within close tolerance limits. Some of this information will assist the designer in deciding upon the location, type, and design of controls to achieve optimum operating conditions. The paper describes in detail the methods adopted for this investigation, and gives the results in graphic and tabular form. A. S.

388. Synthetic detergents in bar form. J. W. McCutcheon. *Soap Sanitary Chem.*, Dec. 1949, **25** (12), 33.—Synthetic detergents in bar form are discussed under toilet and laundry uses, each can be composed of all synthetic detergents or soap plus some synthetic detergent. Costs are discussed: compared with normal toilet soap (86–88% anhydrous), alkyl aryl sulphonates are about 100% higher, which limits their use to about 20%, the alkyl sulphates are more expensive, which limits their use to about 10% of the synthetic bar product. The many characteristics such bar products must conform to, including the physiological and psychological aspects, are outlined, and the advantages and disadvantages are discussed. Eight formulæ are given of toilet products. The main synthetic components being among the following: sodium di-amyl sulphosuccinate, di-sodium *N*-octadecyl sulphosuccinamate, sodium lauryl sulphoacetate, *N*-mono-*n*-butyl urea, *N*-*N*-di-*n*-butyl urea, Igepon, Santamerse, Nacconol, and Duponol. The other components may be: urea, methyl or ethyl cellulose, boric acid, or sodium sulphate. Guanidine carbonate, dicyandiamide, cafeine, ethyl carbonate, alcohol sulphates, sulphated esters, sulphonated amides,

sulphated alkyl ethers are also quoted, but are not shown in the formulæ. The demand for laundry bars has lessened as flakes and granules are more favoured, also soap prices are highly competitive. These are briefly outlined from the detergency efficiency of various forms of anionics, *e.g.*, substituted amides, alkyl aryl sulphonates, etc., and mixtures with soap, non-ionics, cocoanut oil, etc. W. H. C.

389. Toxicity to houseflies of new synthetic pyrethroid. W. A. Gersdorff. *Soap Sanitary Chem.*, Nov. 1949, **25** (11), 129.—The relative toxicity to houseflies of two isomeric forms of a new synthetic preparation related to the pyrethrins has been determined by the turntable method. The compounds tested were kerosine solutions of: (1) a mixture of the esters from the reaction of *dl*-2-allyl-4-hydroxy-3-methyl-2-*cyclo*penten-1-one with *dl-cis-trans*-chrysanthemum monocarboxylic acid, before and after high vacuum distillation and (2) a year-old sample—the isomer prepared from the natural *d-trans* acid, also before and after high vacuum distillation. The standard used for comparison was a kerosine extract of pyrethrum flowers.

The results of the spray tests at difference concn are recorded as the mortality in one day, the concn causing 50% mortality, and the relative toxicity.

The mixture (1) was about three times as toxic as the standard pyrethrum solution. It appears to be about half again as toxic as the separate isomers prepared with either the racemic- *cis* or *trans* acid, but only about half as toxic as the isomer made from the *d-trans* acid.

The isomer (2) was just as toxic as it was a year previously (*J. Econ. Ent.*, 1949, **42** (3), 532–6). Distillation had no effect on the toxicity of either (1) or (2).

W. H. C.

390. The design of experiment. M. G. Evans. *Paint Technol.*, Nov. 1949, **14** (16) 495.—The work of London, Polanyi, and Eyring is briefly discussed. The development of the "stationary state" technique simplified the study of fast reactions. Polanyi's sodium flame reaction, the pyrolysis of alkyl halides, and toluene decomposition are presented. The toluene-decomposition reaction led Szwarte to develop a method for using toluene as the carrier gas when studying other systems, *e.g.*, in the study of $NH_2NH_2 \longrightarrow NH_2 + NH_2$. Free NH_2 radicals react with toluene, forming NH_3, while the benzyl radical dimerizes outside the reaction zone.

Reactions in solution involve experimental methods that are technically easier, but the results are more difficult to interpret. Ingold and Hughes worked in this field. It is stated that solvolysis of halides can occur in two ways, either by a unimolecular dissociation or by a bimolecular ion-exchange reaction.

Polymerization is initiated by hydroxyl groups. Persulphate initiates polymerization, *e.g.*, of vinyl compounds, but oxygen often inhibits the reaction. It was found if a reducing agent was added with the persulphate polymerization occurred more rapidly. A somewhat similar system is the initiation of polymerization by H_2O_2 and $Fe.^{++}$ It was observed that the monomer could act as chain terminator, and different monomers had different degrees of effectiveness. There were three parts to the polymerization reaction: (1) initiation; (2) propagation; (3) termination. This reaction could be used to remove hydroxyl groups, and it throws light on bond energies. Comparisons are drawn between the gas-phase reaction and reaction in solution. The influence of the solvent in the latter type of reaction causes most differences.

To study experimentally reactions of the prototype:

$$Fe^{++} + HO.OH \longrightarrow Fe^{+++} + OH^- + HO$$

a special apparatus was designed, this is briefly described. Interpretation of results and implications are included. D. K.

391. The flow under gravity of a swirling liquid through an orifice-plate. A. M. Binnie and J. F. Davidson. *Proc. Roy. Soc.*, A., **199** (1059), 443–57.—An investigation is described of the whirlpool formed when a swirling liq flows under gravity through a sharp-edged circular orifice from a large reservoir. The velocity distribution in the liq and the shapes of the air-core and the initial part of the emergent jet were determined by the relaxation method. When the swirl was vigorous it was found that, except close to the orifice, the radial and vertical velocities were too small to influence

the shape of the air-core within the tank. Below the orifice the liq was emitted as a conical and rapidly thinning jet. In spite of the contraction at the edge of the orifice, the discharge was not greatly different from that determined by Binnie and Hookings (1948) approx method for flow through a trumpet. Under certain low-swirl conditions the annular jet assumed a cylindrical vibrating form. The theory of these oscillations, which was confirmed by observation, shows that unless the air-core occupies a large fraction of the cross-section of the jet, the wavelength is nearly the same as that in a " solid " jet of the same outer diameter. Two photographs are shown of annular jets with swirl and vibration, and one of the jet without a swirl. W. H. C.

BOOK REVIEW.

Petroleum Production Vol. V. Oil Production by Gas and Flooding. P. J. Jones. New York: Reinhold Publishing Co, 1948. London: Chapman & Hall. Pp. 274 + vii. 48*s*.

This volume is divided into three sections—foundations, oil production by gas, and oil production by flooding.

Again, the first section reviews the concepts developed in earlier volumes which are applicable to displacement of oil by gas and water. The section opens by discussing reservoir characteristics including the effect of reservoir structure and gravity. The pressure–volume–temperature relationships of oil–gas mixtures are discussed, and various volume factors are derived which are applicable to this case. The fundamental theory of flow of oil–gas and oil–water mixtures in porous media is dealt with in some detail. The treatment is again extended to reservoirs of variable permeability, and the effect of gravitational migration is considered. Equations are developed for determining gas–oil and water–oil ratios under various operating conditions. The case of combined displacement of oil by gas and water is also considered. The separation of oil–gas mixtures at the surface and of vaporization in the reservoir with declining reservoir pressure are discussed at length: the discussion is based on fundamental pressure–volume–temperature relationships and the variation of equilibrium constants with pressure and temperature. The effect of pressure maintenance by gas injection is also considered.

In the second section these principles are applied in turn to the production of oil by gas displacement from two hypothetical radial reservoirs (referred to as the R-10 and R-11 reservoirs), and to one hypothetical linear reservoir (referred to as the L-10 reservoir).

In the third section the principles are applied to a discussion of the economics of flooding by water.

A useful appendix of tables is presented showing the variation of equilibrium constant with temperature and pressure for various fractions up to and including heptanes and heavier.

As in the previous volumes of the series the treatment is thorough, but the continued repetition of fundamentals tends to make it rather difficult to follow the theme of the development. Whilst the treatment is purely theoretical, no actual reservoir performance data being quoted, it represents the nearest approach which can be achieved at the present time to the prediction, on purely theoretical grounds, of the behaviour of oil reservoirs.

R. B. S.

APPLICATIONS FOR MEMBERSHIP OR TRANSFER.

FEBRUARY 1950.

The following have applied for admission or transfer to the Institute. In accordance with the By-laws, the proposals will not be considered until the lapse of at least one month after the publication of this *Journal*, during which time any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of the candidates.

The object of this information is to assist the Council in grading the candidate according to the class of membership.

The names of candidates' proposers and seconders are given in parentheses.

Applications for Membership.

CUSACK, John Gilbert, refinery supervision trainee, Trinidad Leaseholds Ltd.

EASTLAKE, Arthur Lloyd, technologist, Sinclair Refinery Co. (*G. Sell ; E. L. Lomax.*)

EATWELL, Horace John, engineer, Anglo-Iranian Oil Co. Ltd. (*R. Stansfield ; J. G. Withers.*)

FLATOW, George Joseph Fritz, general manager and chief engineer, Oil Department, Amber Chemical Co. (*E. W. Steinitz ; T. J. Metcalf.*)

GREEN, Thomas Saunders, industrial sales engineer, Anglo-American Oil Co. Ltd. (*W. E. J. Broom ; C. Chilvers.*)

HARRIS, Eric Victor, clerk, Messrs John Hudson & Co. Ltd. (*W. J. Crafter ; A. Jackson.*)

KELLY, Winfield Hamilton, Regular Army Officer, R.A.S.C. (*P. F. Ellis ; E. J. Horley.*)

KEMP, John Norman, chemist, Anglo-American Oil Co. Ltd. (*R. G. Protheroe ; L. H. Cowell.*)

LEONARD, Julian Maynard, joint managing director, Messrs Carless, Capel & Leonard Ltd. (*J. A. Oriel ; S. J. M. Auld.*)

MARRIOTT, Anthony Lawson Carr, Chief Petrol and Supply Officer, R.A.S.C. (*E. J. Horley ; P. F. Ellis.*)

MARTIN, Frank Percy, lubricant research engineer, Messrs Alexander Duckham & Co. Ltd. (*A. C. Pepper ; P. Driver.*)

MOINUDDIN, Mohamed, Lieutenant, R.A.S.C. (*E. J. Horley ; P. F. Ellis.*)

SANDERSON, Robert Frederick, Officer, R.A.S.C. (*E. J. Horley ; P. F. Ellis.*)

SAWHNEY, Dewan Indar Sain, Staff Captain, R.I.A.S.C. (*P. F. Ellis ; E. J. Horley.*)

SILL, Silvester Anthony, Officer, R.A.S.C. (*P. F. Ellis ; E. J. Horley.*)

WALLERSTEINER, William Kurt Samuel, technical director, Watford Chemical Co. Ltd. (*L. Ivanovszky ; Dr. O. Tokayer.*)

WOOLNOUGH, Eric, Drawing Office and Construction Dept., National Oil Refineries Ltd. (*H. Murphy ; E. J. Horley.*)

Transfers.

DAVIS, Alec Kenneth, works chemist, "Shell" Refining and Marketing Co. Ltd. (*I. A. B. Pender ; R. R. Ferner.*) (*Transfer from Student to Associate Member.*)

FIRTH, William Ward, senior works chemist, "Shell" Refining and Marketing Co. Ltd. (*H. E. F. Pracy ; H. W. Fleming.*) (*Transfer from Member to Associate Fellow.*)

NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws.

Elections are subject to confirmation in accordance with the By-Laws.

As Fellows.

GUNTHER, A. E. MAPSTONE, G. E.

As Members.

NAGHAVI, S. NIEL, W. H.

As Associate Fellows.

ALLAN, R.	HARVEY, C. W.	ROMAN, W.
BLACKMORE, D. S.	HOLDING, A. E.	SCALLAN, J. E. P.
BRITTAIN, E. W.	JEFFERS, J. E. M.	SMETHURST, N. B.
BRUTON, H. S.	KEEL, C. L.	SPEAR, P.
DAVIES, A.	KRISHNAMURTHI, C. R.	TOWNEND, P. V.
GLYNN, F. J.	OWEN, H. E. R.	WHITE, N. A.
HALL, F.	PARKS, N. E.	WINSCOMBE, J. E.
HARRIS, W. R.	PATE, W.	

As Associate Members.

BROOKS, G. E.	CUNNAH, E.	MACDONALD, R.
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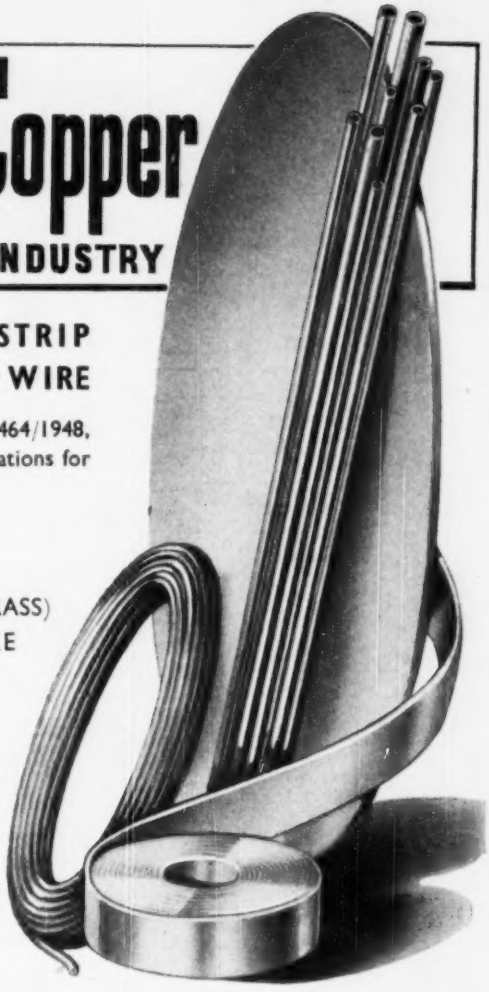

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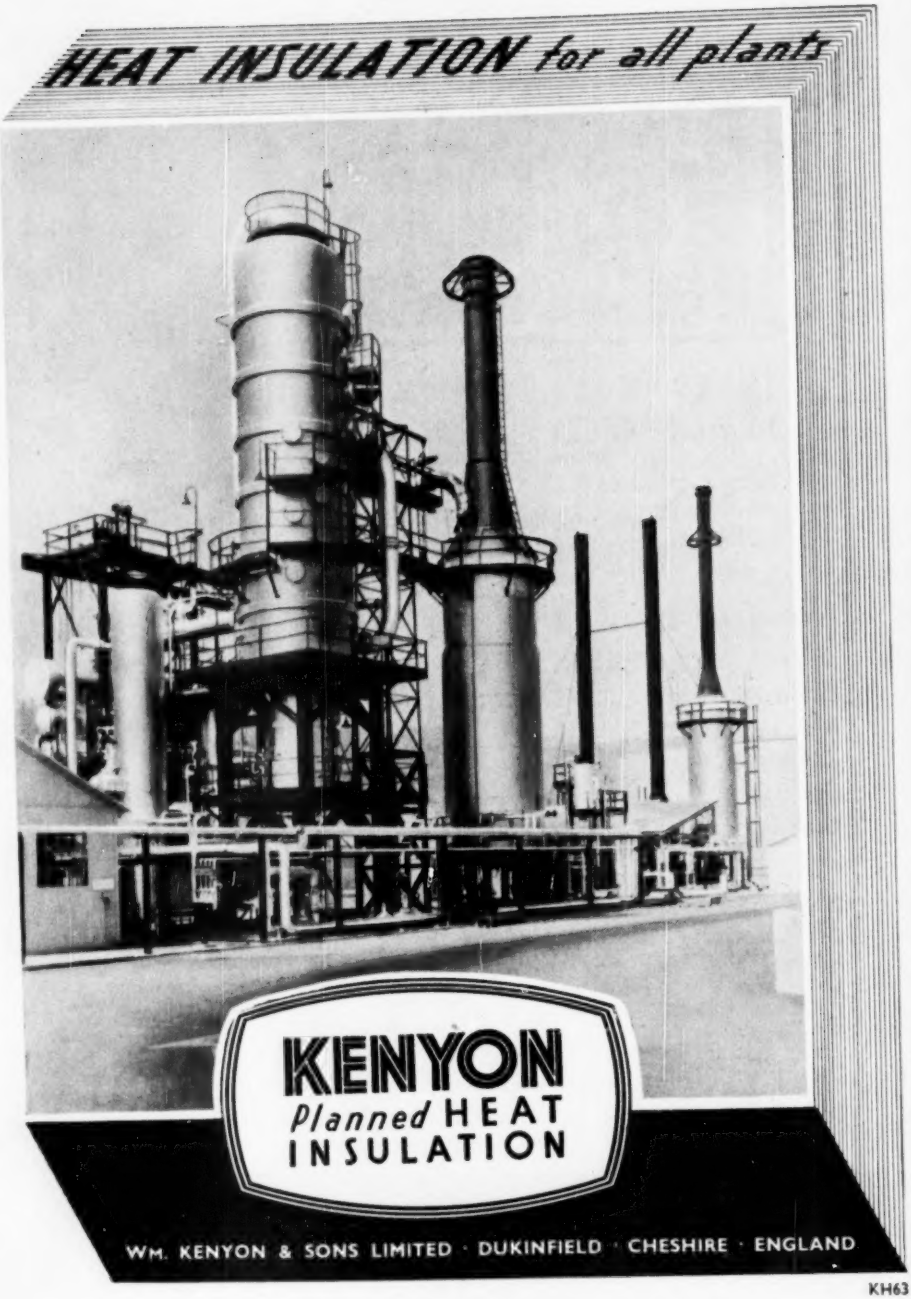

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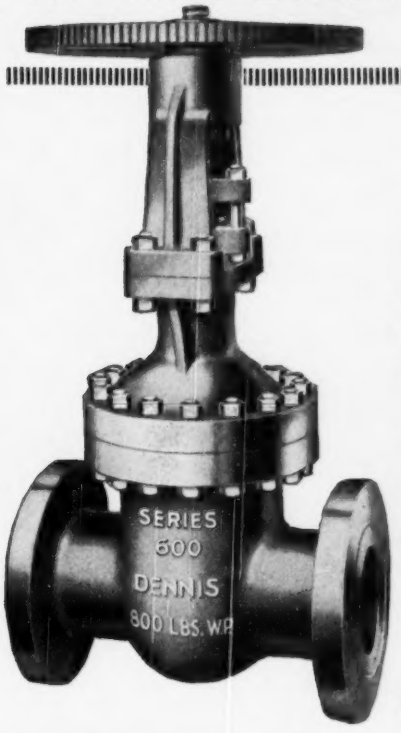

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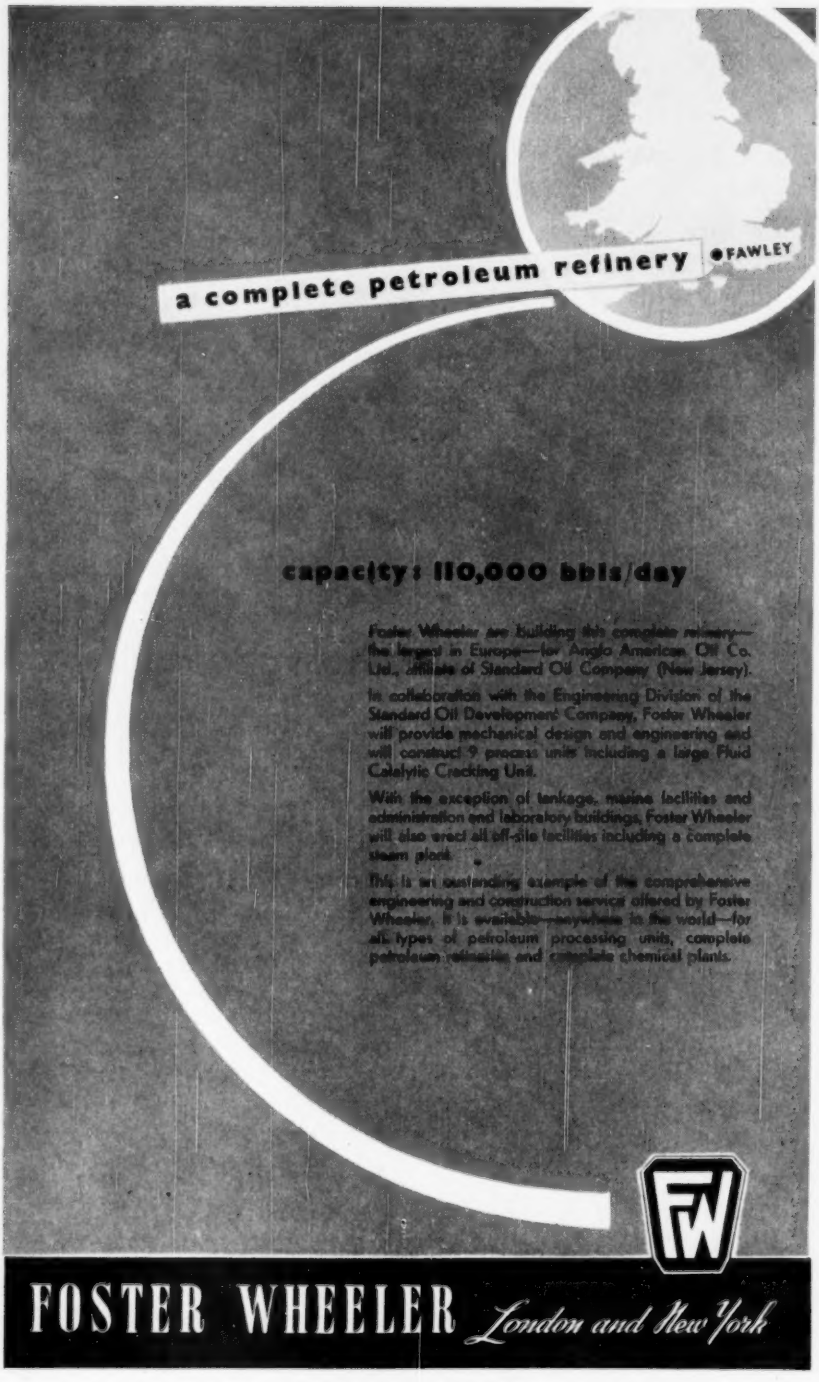
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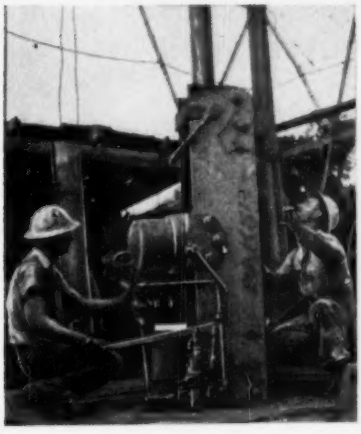

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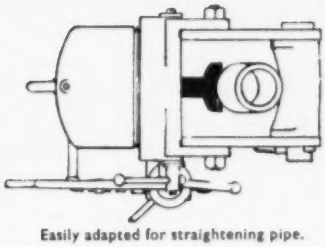

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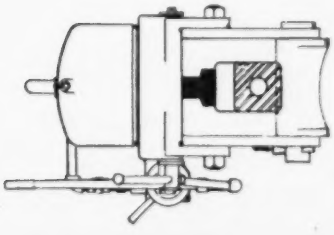

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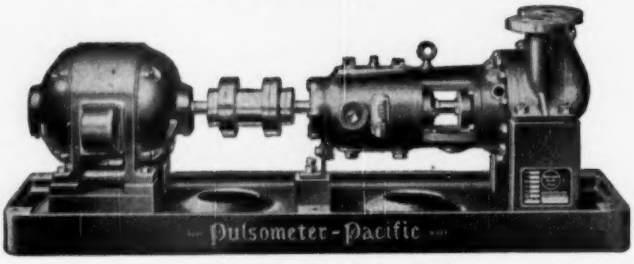

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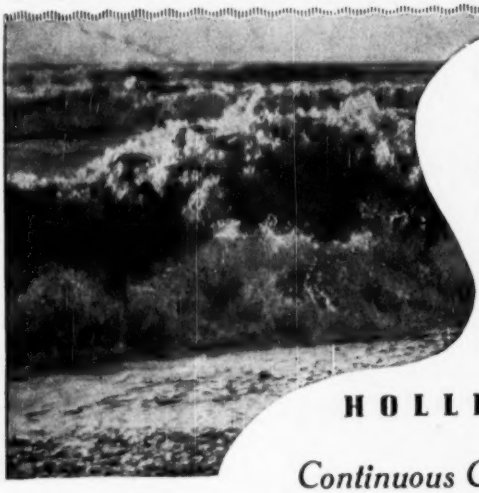

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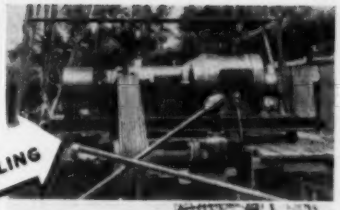

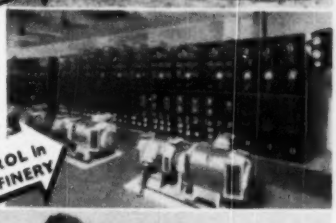

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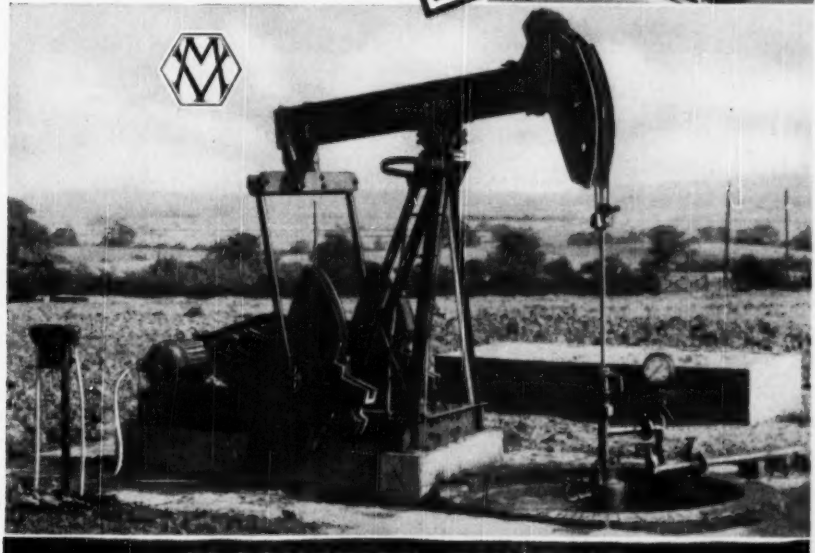

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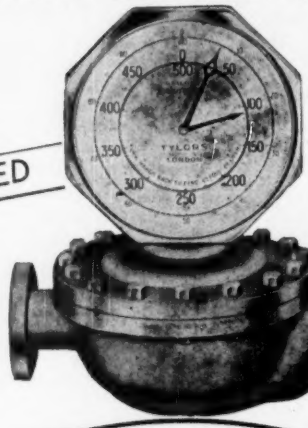

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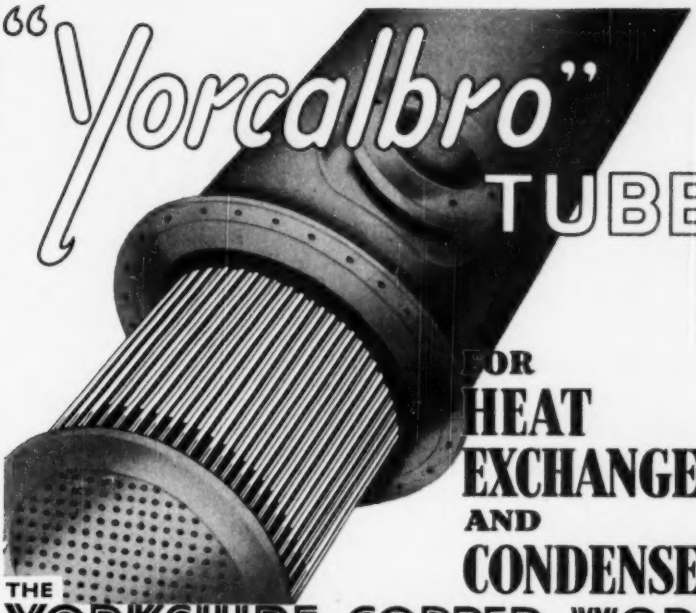

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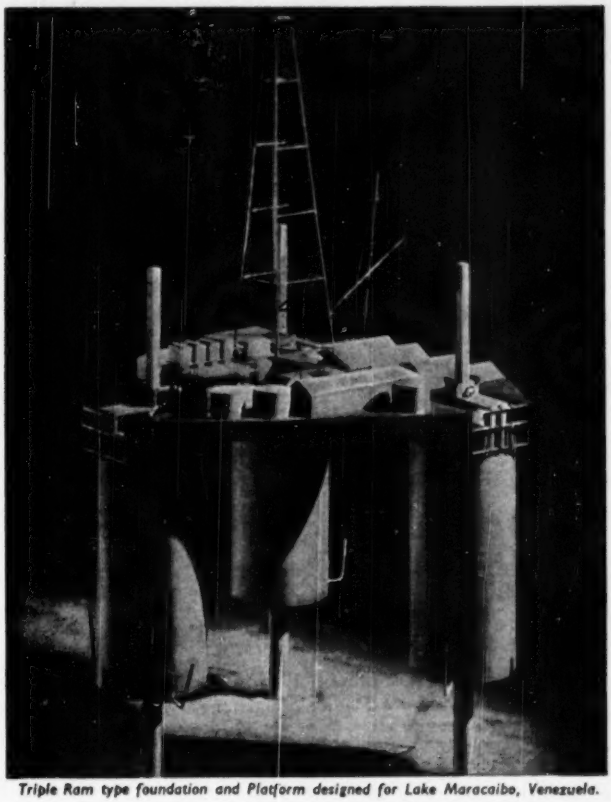

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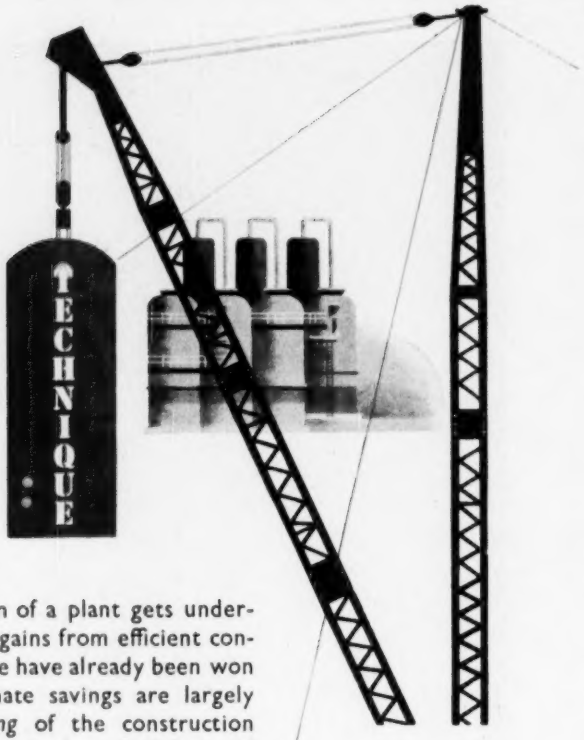

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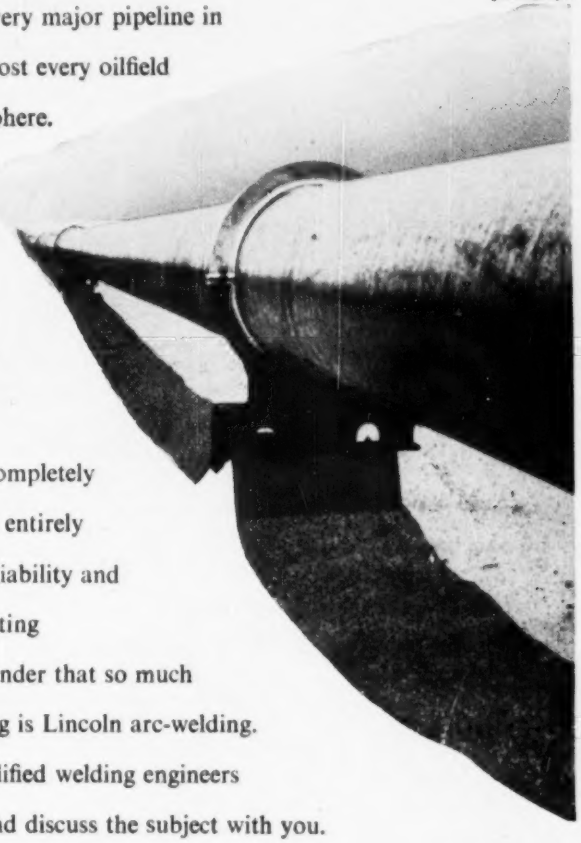

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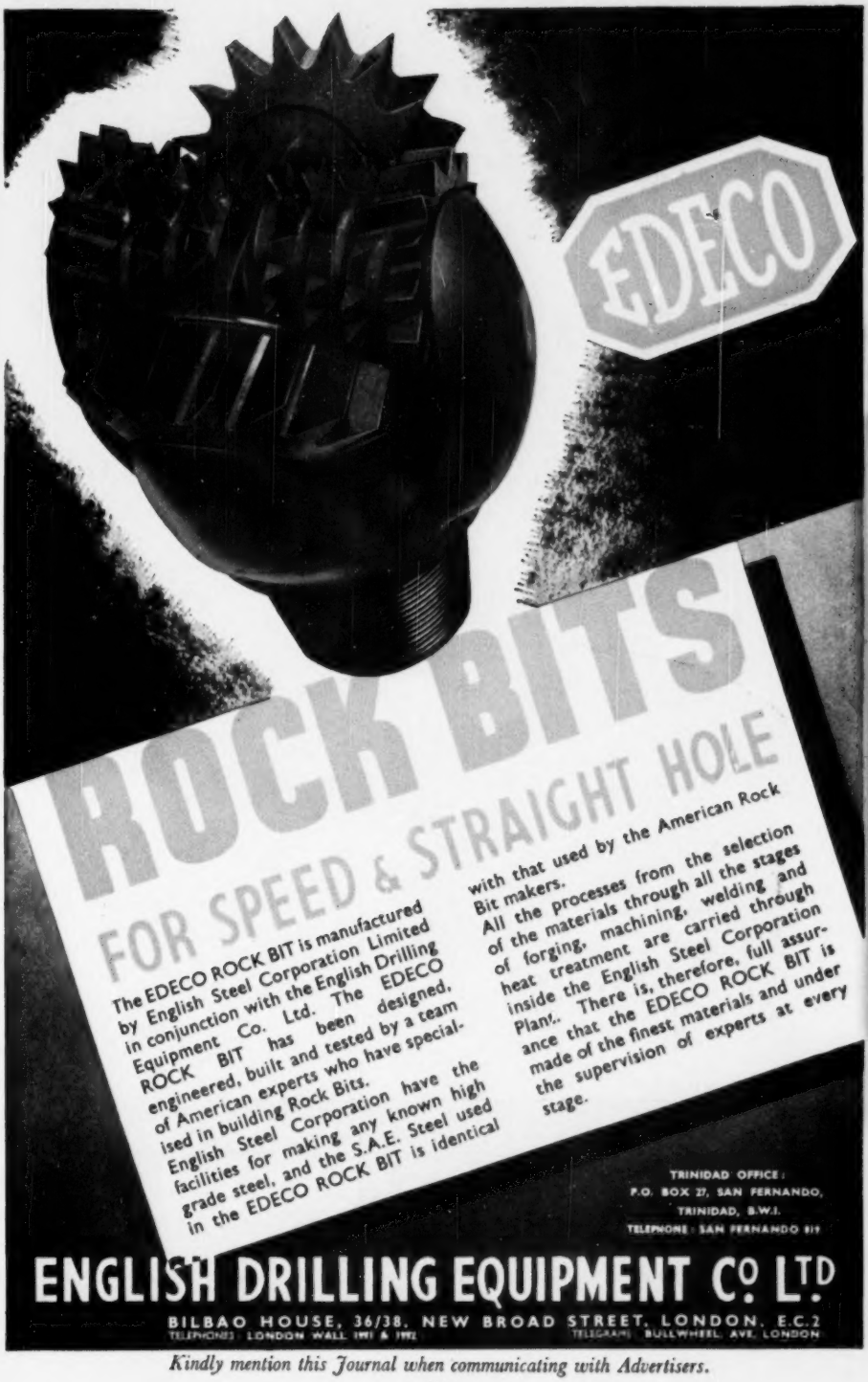
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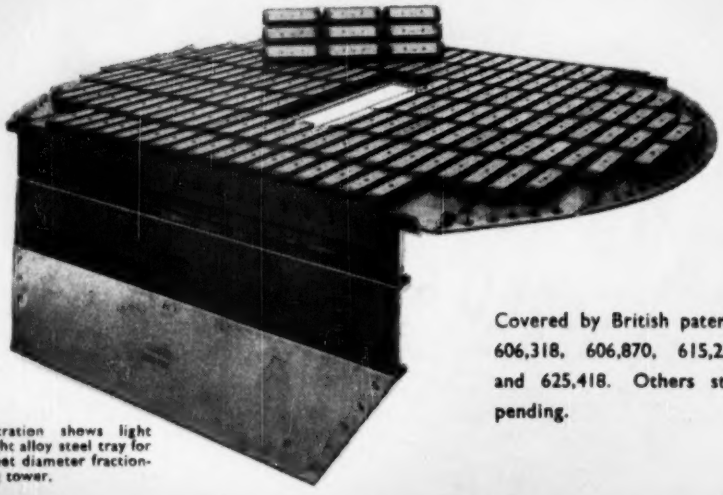

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